



12502

92

JOURNAL
OF
THE CHEMICAL SOCIETY.

TRANSACTIONS.

Committee of Publication:

- | | |
|--------------------------------------|---|
| HORACE T. BROWN, LL.D., F.R.S. | A. MCKENZIE, M.A., D.Sc., Ph.D. |
| A. W. CROSSLEY, D.Sc., Ph.D., F.R.S. | R. MELDOLA, F.R.S. |
| H. B. DIXON, M.A., F.R.S. | G. T. MORGAN, D.Sc. |
| WYNDHAM R. DUNSTAN, M.A., F.R.S. | A. SCOTT, M.A., D.Sc., F.R.S. |
| M. O. FORSTER, D.Sc., Ph.D., F.R.S. | Sir EDWARD THORPE, C.B., LL.D.,
F.R.S. |
| C. E. GROVES, F.R.S. | |
| J. T. HEWITT, M.A., D.Sc., Ph.D. | |

Editor:

J. C. CAIN, D.Sc., Ph.D.

Sub-Editor:

A. J. GREENAWAY.

1909. Vol. XCV. Part II.

102287
7/6/10

LONDON:

GURNEY & JACKSON, 10, PATERNOSTER ROW.
1909.

RICHARD CLAY & SONS, LIMITED,
BREAD STREET HILL, E.C., AND
BUNGAY, SUFFOLK.

QD

1

C6

v.95

pt.2

cop 3

A sample of this substance kept in a sealed tube was still almost white a week after preparation, thereafter the yellow colour slowly became more marked. On opening the tube, sulphur, sulphur dioxide, and *p*-toluic anhydride were found to be present. The anhydride was identified by a determination of its melting point and by conversion into *p*-toluic acid.

CHEMISTRY DEPARTMENT,
THE GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

CXXXIX.—*The Velocity of Decomposition of Nitro-glycerin by Heat. Part I.*

By ROBERT ROBERTSON, M.A., D.Sc., F.I.C.

ALTHOUGH the decomposition of nitrocellulose at temperatures below the explosion point had long been a familiar phenomenon, the mechanism by which the removal of nitrogen from the nitric ester takes place was not investigated until recently, when Dr. Will gave the results of his experiments in two papers: "Untersuchungen über die Stabilität von Nitrocellulose" (Erste und Zweite Mitteilungen aus der Zentralstelle für Wissenschaftlich-technische Untersuchungen). In these papers the method of research is founded on the measurement of the nitrogen evolved in unit time from the nitrocellulose when this is heated at definite temperatures under such conditions that the volatile products of decomposition are continuously removed. From the results obtained many important deductions are made, of which, perhaps, the principal is that a normal or intrinsic decomposition is a fundamental property of cellulose nitric esters, among which is gun-cotton. For a given temperature this normal decomposition is characterised by a uniformity of evolution of nitrogen, on the one hand, and by a certain minimum of evolution, depending on the degree of nitration of the cellulose, on the other. Instability may be detected by irregularity in decomposition, or by a higher coefficient of evolved nitrogen than is found with nitrocelluloses purified until they have reached their limiting state of minimum evolution.

The dependence on temperature of the intrinsic evolution of nitrogen from fully purified nitrocellulose has been worked out by Will, who gives an equation expressing the quantity of nitrogen disengaged as a function of the temperature. From this he calculates by exterpola-

tion values for the disengagement of nitrogen from nitrocellulose at the ordinary temperature.

Will also discusses the nature of the decomposition of guncotton, and draws the conclusion that the volatile nitrogenous gases evolved consist for the most part of nitric oxide.

This view is not confirmed by a long series of experiments, in which it is proved that not only under the conditions of the Will test, but also in a vacuum and under other methods of treatment, the nitrogen is evolved from normal guncotton to a large extent in the form of nitric peroxide. The nitrogen in the latter form, in which it was estimated by a specially worked out process of quantitative spectroscopic measurement of that gas, exists, indeed, under the continuous removal of volatile products of the Will test, to the extent of more than 40 per cent. of the total nitrogen (Robertson and Napper, *Trans.*, 1907, **91**, 761, 764).

Decomposition of Nitroglycerin (Glyceryl Trinitrate).

There is no previous knowledge of the mode of decomposition or real stability of nitroglycerin, and its liability to such a process of decomposition as has been shown to exist for nitrocellulose has always been doubtful, especially in view of the obvious difference between crystalloidal nitroglycerin—a compound of known molecular weight and definite constitution—and the corresponding nitric ester of cellulose, of which the molecular weight is very high and the constitution unknown.

The matter has remained in this condition for several reasons, among which may be mentioned experimental difficulties connected with the volatility of nitroglycerin when subjected to any process of heating, and doubtless also the risks involved in dealing with this substance at temperatures above the normal.

These difficulties have now been overcome to a great extent, and an apparatus (Fig. 1) has been devised for investigating the mode of decomposition of nitroglycerin without loss of that somewhat volatile substance from the experimental system, and also without danger.

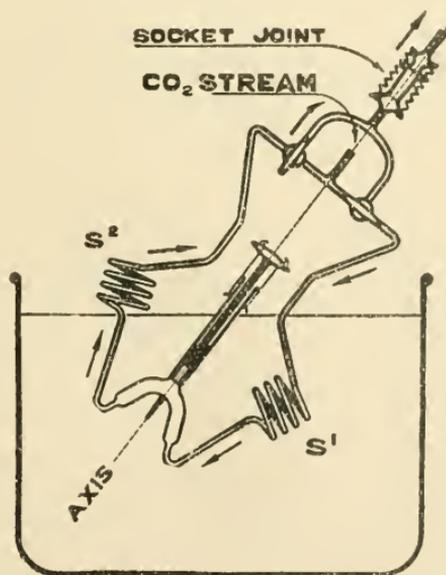
It may be stated at the outset that the results of the experiments conclusively show that nitroglycerin, as well as the cellulose nitric esters, undergoes an intrinsic decomposition, which is a function of the temperature and is a fundamental property of the substance.

A description of the experimental methods and the results obtained, together with a comparison of the latter with those given by guncotton, are given below.

EXPERIMENTAL.

A. *Apparatus*.—The apparatus used for the decomposition is shown in Fig. 1. Glass wool, made from Jena glass, impregnated by soaking with 0.3 to 5.0 grams of nitroglycerin, is introduced into the horse-shoe-shaped tube by means of the aperture fitted with a ground-in glass plug, which is slightly greased with a non-reactive oil and further sealed with mercury. By means of the glasscocks shown in the drawing, the current of carbon dioxide can be directed so that it either passes down the right-hand spiral, through the glass wool impregnated with nitroglycerin and up the other spiral, or vice versa.

FIG. 1.

*Decomposition vessel for nitroglycerin.*

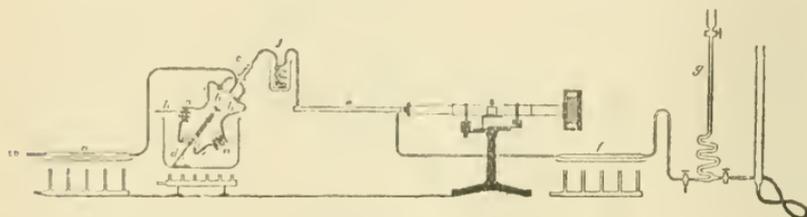
At one end of the apparatus is a slip-joint, so that the whole system can be rotated on its axis. The point shown in the centre of the horse-shoe is in the axis, and forms a supporting pivot.

The method of using the apparatus is clear from Fig. 2, which gives the arrangement for one of the experiments.

The stream of carbon dioxide used for these experiments was specially pure, and contained only 0.02 per cent. of gas unabsorbed by potassium hydroxide solution. To prevent even the possibility of the presence of oxygen, this carbon dioxide was passed over red hot copper asbestos (Kreusler's) in *a*, and thence to the apparatus. When the taps are open, as shown at *b*₁ and *b*₂, the stream of gas is passed

through spiral s_1 , which is immersed in an oil-bath, the temperature of which is known, and is maintained uniform by a stirrer (not shown); after traversing the glass wool impregnated with nitroglycerin, it passes into spiral s_2 , which is outside the heated oil, is protected from radiation of heat from the oil by asbestos cards, and has impinging on it a blast of cold air, h . In this way any nitroglycerin that has been volatilised in the current of carbon dioxide is condensed in spiral s_2 . After a certain period (for example, half an hour), the whole apparatus is rotated through 180° on its main axis, the two fixed points being the slip-joint, c , and the pivot, d . The spiral, s_1 , cooled by the air blast, now becomes the condenser of nitroglycerin, and any nitroglycerin which has been condensed in s_1 is now returned to the heated system. The spiral under the surface of the oil serves also as a pre-heating worm, in traversing which the carbon dioxide is gradually raised to the proper temperature of experiment. By means of this arrangement, fixed glass tubes can be led from the rotating joint to any apparatus for examining or measuring the gases, and the use of

FIG. 2.



Apparatus for estimating NO_2 and total N from nitroglycerin.

rubber tubes, which are liable to attack by the nitrogenous gases, is avoided. After the lapse of another period, the apparatus is again rotated, when the spirals assume their reciprocal functions.

As a further precaution against the carrying over of nitroglycerin, the gases pass through an ice-cooled worm, j , immediately on leaving the decomposition apparatus. The interposition of this worm has no effect on the estimation of nitrogen existing as nitric peroxide.

After traversing the apparatus, the carbon dioxide, carrying with it the volatile products, was examined in a number of ways. In all cases, however, it was passed through an observation tube, e , and during its passage through this the concentration of nitric peroxide was estimated by the spectroscopic method of Robertson and Napper (*loc. cit.*). From the concentration of nitric peroxide, the weight of nitrogen disengaged in this form was calculated. In most of the experiments the gas, after traversing the observation tube, was led through a combustion furnace (f), fitted with both reduced copper asbestos, to reduce all the nitrogenous gases to nitrogen, and also with some copper oxide

asbestos to oxidise any carbonaceous gases to carbon dioxide, for absorption in the potassium hydroxide solution contained in the measuring burette (*g*). In the latter, the unabsorbed gases are read off every quarter of an hour, and calculated to weight of nitrogen after deducting the previously determined nitrogen correction in the stream of carbon dioxide, the rate of which was kept uniformly at 1000 c.c. per hour.

B. *Results*.—(1) The disengagement of nitrogen proceeds in a perfectly uniform manner. This is apparent from table I, which shows the concentration of nitric peroxide estimated spectroscopically, and the volume of nitrogen disengaged per quarter of an hour for a period of four hours.

TABLE I.

Decomposition of Nitroglycerin in a Current of Carbon Dioxide at 120°.
(0.5 gram of Nitroglycerin.)

Rate of Carbon Dioxide Stream = 1000 c.c. per hour.

Quarter hour.	Concentration of NO ₂ gas in CO ₂ stream, spectroscopically estimated per cent. by volume.	C.c. of N ₂ after combustion, unabsorbed by potash solution, less nitrogen correction of the CO ₂ .	Quarter hour.	Concentration of NO ₂ gas in CO ₂ stream, spectroscopically estimated per cent. by volume.	C.c. of N ₂ after combustion, unabsorbed by potash solution, less nitrogen correction of the CO ₂ .
1	0.04	0.05	9	0.13	0.15
2	0.07	0.15	10	0.13	0.10
3	0.09	0.15	11	0.12	0.15
4	0.11	0.15	12	0.12	0.10
5	0.11	0.15	13	0.12	0.15
6	0.12	0.15	14	0.12	0.15
7	0.12	0.15	15	0.12	0.10
8	0.12	0.15	16	0.12	0.15

(2) The nitrogen is disengaged from nitroglycerin as nitric peroxide.

(a) It will be seen from the results given in table II, throughout a considerable range of temperature, that agreement is obtained between the total quantity of nitrogen evolved as estimated by a Dumas combustion and the nitrogen estimated spectroscopically in the form of nitric peroxide.

In the same table are also given, for the sake of comparison, the corresponding figures for guncotton according to (i) the exponential formula given by Will (*Zweite Mitt.*, p. 26), and (ii) a temperature-coefficient of 2 for 5° (compare Brunswig, *Explosivstoffe*, 1909, p. 29).

TABLE II.

Disengagement of Nitrogen from 2.5 grams.

Temperature.	Nitroglycerin.		Guncotton.			
	Total N (by combustion).	N as NO ₂ (by spectroscopic observation).	Total N (method i).	Total N (method ii).	N as NO ₂ (R. & N.*)	
135.0°	4.87	4.33	0.55	0.55	0.23	
130.0	2.72	2.90	0.26	0.27	—	
124.9	1.62	1.57	0.12	0.14	—	
119.8	0.74	0.80	0.055	} Interpolated values. {	—	
115.0	0.36	0.39	0.026		0.07	—
110.2	0.20	0.20	0.011		0.034	—
105.0	0.10	0.086	0.005		0.017	—
100.5	0.044	0.043	0.002		0.008	—
95.0	0.021	0.024	0.0008		0.004	—
90.3	0.009	0.010	0.0003		0.002	—
					0.001	—

* Trans., 1907, 91, 775.

(b) When the gases from the observation tube are led directly into potassium hydroxide, in which all the nitric peroxide would be absorbed together with as much nitric oxide as would combine to form nitrogen trioxide, no nitric oxide is ever obtained. There is therefore no nitric oxide gas over and above the quantity required for the equation $\text{NO} + \text{NO}_2 = \text{N}_2\text{O}_3$.

(c) An analytical confirmation of the evolution of nitric peroxide was obtained by leading the gases from the decomposition tube first through the observation tube and then into bulbs containing sulphuric acid. The latter was then shaken up in a nitrometer, and the nitrogen existing as nitric peroxide calculated from the nitric oxide obtained. The results showed that the figure thus obtained agreed with the figure from spectroscopic observation, being slightly lower on account of the inclusion of the initial period before the constant disengagement is established, thus :

	From 2.5 grams of nitroglycerin per qr. hour mg. N ₂ .
N as NO ₂ estimated spectroscopically (at constant evolution).....	1.32
N as NO ₂ absorbed by H ₂ SO ₄ (average of 16 quarters)	1.45

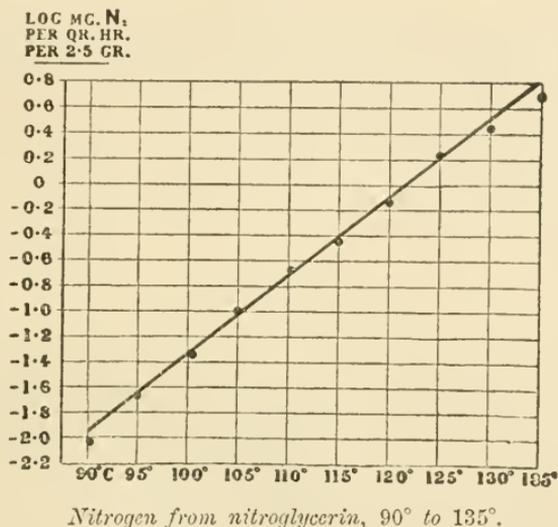
(3) The rate of disengagement of nitrogen is markedly increased by rise in temperature.

In Fig. 3 are plotted temperatures and logarithms of disengagement of nitrogen from the results given in table II. It will be seen that between the temperatures of 95° and 125° the results fall on a straight line.

From the rise in the logarithms a temperature-coefficient of 2 for 5° is indicated throughout this range for increase in disengagement of nitrogen from nitroglycerin.

(4) The quantity of nitrogen disengaged from nitroglycerin exceeds that from guncotton when these two substances are treated under similar conditions, that is, on heating, with removal of catalytic volatile products of decomposition. This is evident from table II, where the observed results from nitroglycerin are compared with those given by guncotton, the disengagement from the latter being calculated by extrapolation according to both methods (i and ii on page 1245).

FIG. 3.



By the method of hydrolysis, also, Silberrad and Farmer (Trans., 1906, 89, 1759) found the rate of hydrolysis of nitroglycerin to be much higher than that of guncotton.

Conclusions.

The decomposition of nitroglycerin with continuous removal of volatile products has been studied at temperatures of 90° and upwards, and the following conclusions are made from the results obtained.

(1) In a suitable apparatus the decomposition of nitroglycerin proceeds in a manner as uniform as that of a stable guncotton when the volatile products of decomposition are continuously removed.

(2) The nitrogen is disengaged for the most part, if not entirely, as nitric peroxide, and the estimation of the nitrogen existing as such by the spectroscopic method agrees with the results of estimation by combustion and other methods. In this respect nitroglycerin differs from guncotton, from which the nitrogen disengaged as nitric peroxide at 135° amounts to only about 40 per cent. of the total nitrogen.

(3) The rate of decomposition is a function of the temperature, and increases from 95° to 125°, being doubled in a rise of 5°.

(4) Nitroglycerin has a higher rate of decomposition than guncotton under similar conditions and at the same temperature.

As the spectroscopic method is capable of estimating nitric peroxide in even smaller concentrations than those already dealt with, further work is in progress to determine the manner of the decomposition of nitroglycerin at still lower temperatures without having recourse to extrapolation.

In conclusion I have to thank Colonel Sir F. L. Nathan and Major J. H. Mansell, R.A., for their interest in this work, and the Director of Artillery for permission to publish the results.

RESEARCH DEPARTMENT,
ROYAL ARSENAL,
WOOLWICH.

CXL.—*The Oxidation of Mucic Acid in Presence of Iron.*

By FREDERIC FERRABOSCHI.

It has been shown by Fenton (Trans., 1894, 65, 899; 1895, 67, 48; 1896, 69, 546; 1898, 71, 167, 472; *Brit. Assoc. Reports*, 1895, 1898, 1899, etc.) that various interesting oxidations can be effected in presence of traces of ferrous iron as catalyst.

Fenton and Jones (Trans., 1900, 77, 76), in a general investigation on the oxidation of various acids by means of hydrogen dioxide in presence of iron, showed that mucic and saccharic acids on oxidation yielded solutions which gave a deep reddish-violet colour with ferric chloride and sodium hydroxide, and a precipitate with phenylhydrazine. The products of oxidation were stated to be very unstable, and were not isolated or further examined.

An attempt to undertake such an examination has now been made at Dr. Fenton's suggestion.

The oxidation of mucic acid was first investigated, and then parallel experiments were made with saccharic acid.

The following method was generally adopted for the oxidation. Mucic acid was boiled with a considerable volume of water, and a solution of the lactone acid ("paramucic acid") thereby obtained (Fischer, *Ber.*, 1891, 24, 2136). A small quantity of pure metallic

iron ("ferrum redactum,"—about 0.05—0.1 gram for every 10 grams of mucic acid) was then dissolved in the solution. After cooling, hydrogen dioxido (20 volumes) was added slowly, in the proportions of $1\frac{1}{2}$ —2 molecules of dioxide to one of the acid. Each addition of hydrogen dioxido produced a deep brown coloration, which gradually faded, and the next addition was not made until the colour had disappeared. The oxidation was carried out at the ordinary temperature, the large volume of water preventing any appreciable rise in temperature.

The solution obtained after oxidation gave as its most characteristic reactions: *Ferric chloride, followed by sodium hydroxide.*—Deep reddish-purple colour, bleached by dilute sulphuric acid. *Phenylhydrazine acetate.*—Orange precipitate, increasing on keeping.

Unaltered paramucic acid was always found to be present, its entire oxidation not being effected even when a considerable excess of hydrogen dioxido was used.

Action of Phenylhydrazine.

Phenylhydrazine acetate (about 1 molecule for each molecule of hydrogen dioxido used) was added to the solution obtained after oxidation. An orange-coloured precipitate was produced, the quantity of which increased considerably on keeping at the ordinary temperature. After about forty hours the precipitate was collected.

It was a matter of considerable difficulty to obtain the substance in a state of purity. Crystallisation from most of the ordinary solvents was tried without success, the method finally adopted being the following. The substance was dissolved in excess of hot sodium carbonate solution, the sodium salt being much more soluble than the dihydrazone acid itself. Dilute hydrochloric acid was then added, when the dihydrazone was again precipitated. It was collected and dried at 100°. Hot saturated solutions in alcohol and toluene were then made, and the two mixed. The dihydrazone was deposited from the mixture, on cooling, in minute, bright yellow needles, melting and decomposing at 256° (quick heating).

The substance dissolves readily in benzene, toluene, or pyridine, is less soluble in alcohol, ether, or chloroform, and only very slightly so in water:

0.1920 gave 0.4148 CO₂ and 0.0744 H₂O. C = 58.92; H = 4.31.

0.1223 ,, 15.75 c.c. N₂ at 14° and 761 mm. N = 15.3.

C₁₈H₁₆O₅N₄ requires C = 58.70; H = 4.35; N = 15.2 per cent.

The compound would therefore appear to be the dihydrazone (or osazone) of an oxidation product of mucic acid, minus a molecule of

water, its formula having either a lactone ring (I) or a pyrazolone ring (II).



With the view of deciding between the two possibilities, the substance was titrated at about 40° against a solution of baryta, using phenolphthalein as indicator. If the pyrazolone formula were correct, it should act as a monobasic acid, whilst if the substance had the lactone formula, it might, in presence of a base, act as a dibasic acid:

0.1477 of pure crystallised oxalic acid required 18.4 c.c. of the baryta solution. 0.1903 of the substance required 8.3 c.c.

Calculated for lactone formula, 8.12 c.c.

Calculated for pyrazolone formula, 4.06 c.c.

The substance would, therefore, appear to have a lactone formula, as represented above (I).

Action of Hydrogen Chloride on the Dihydrazone in Alcoholic Solution.

The dihydrazone was dissolved in absolute alcohol, and the solution saturated with dry hydrogen chloride. The liquid thus obtained yielded on evaporation clusters of bright orange-coloured needles, melting at 158° (quick heating) to a deep orange-red liquid. After twice recrystallising from alcohol, no change in melting point was observed, and the substance was therefore regarded as pure:

I. 0.0979 gave 0.2114 CO₂ and 0.0451 H₂O. C = 58.88; H = 5.12.

II. 0.1510 „ 0.3253 CO₂ „ 0.0689 H₂O. C = 58.75; H = 5.11.

III. 0.1820 „ 23.8 c.c. N₂ at 16° and 749.4 mm. N = 15.2.

From the following reasons the substance appears to be an ester derived from the dihydrazone.

(1) It does not dissolve readily in sodium carbonate solution in the cold, but dissolves easily on warming. On adding dilute hydrochloric acid to this solution, a precipitate is obtained which proves to be the original dihydrazone.

(2) On digesting under reflux with sodium hydroxide and then distilling, ethyl alcohol was found in the distillate, and recognised by the iodoform reaction and by oxidation to acetaldehyde.

On account of the numerical approximation between the compositions calculated for various ester-formulae, it is not possible, from the analytical figures, to assign to it a definite constitution.

Dihydroxymucic Acid.

With the view of isolating the products of oxidation, the solution resulting after the oxidation of paramucic acid was evaporated at about 60—80° to a syrup. Darkening in colour always occurred during the process. The syrup was then extracted several times with alcohol. The alcoholic solution gave the characteristic reactions with ferric chloride and phenylhydrazine acetate, and reduced ammoniacal silver nitrate and Fehling's solution very strongly. It contained a considerable quantity of a substance which appeared, for reasons discussed at the end of this paper, to be ethyl hydrogen mucate. This was, to a large extent but not entirely, precipitated by adding to the solution several times its own volume of ether; most of the iron, which was still present in traces, being carried down at the same time. The filtrate, after concentration to a syrup in a vacuum over sulphuric acid, deposited in the course of several days crystals of an acid which was found to have very strong reducing properties.

The above method of isolating the acid only yielded it in very small amount. An attempt was therefore made to isolate it from its lead salt. The lead salt, mixed with lead mucate, was precipitated by addition of lead acetate to the solution obtained after the oxidation. The mixed lead salts were suspended in ether, into which hydrogen sulphide was then passed. Since mucic acid is insoluble in ether, this process effected the separation of the oxidation product from the unaltered mucic acid. The ethereal solution was evaporated in a vacuum, and yielded a syrup which slowly deposited crystals of the acid.

The acid was found to be soluble in water, alcohol, or acetone, and less soluble in ether; it melted and decomposed at 205—207°. In aqueous solution it instantly reduced ammoniacal silver nitrate in the cold, and reduced Fehling's solution in the cold or on very slightly warming. With ferric chloride, no coloration was produced, and on subsequently adding sodium hydroxide, a precipitate of ferrous hydroxide was formed.

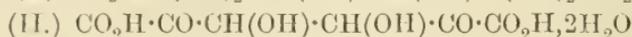
It is obvious from these facts that the oxidation must yield at least two products, since the substance isolated does not give the colour reaction with ferric chloride which is characteristic of the solution obtained after oxidation.

Owing to the instability of the product, it was only obtained in very small amount. It has therefore not yet been possible to prepare by recrystallisation a sample sufficiently pure for very accurate analysis. A specimen which had not been recrystallised gave the following figures:

0.1225 gave 0.1373 CO_2 and 0.0459 H_2O . $\text{C} = 30.57$; $\text{H} = 4.20$.

Mucic acid, $\text{C}_6\text{H}_{10}\text{O}_5$, + 2O requires $\text{C} = 29.75$; $\text{H} = 4.17$ per cent.

The substance therefore appears to be a *dihydroxymucic acid*, its constitution, as appears below, being probably represented by the formula (I), and to react with phenylhydrazine as *dihydroxydiketo-*



adipic acid (II), yielding the dihydrazone, which has been prepared.

Oxidation of Saccharic Acid in Presence of Iron.

It is obvious that further light could be thrown on the constitution of the products of oxidation by examining whether or not saccharic acid yielded products identical with those obtained from mucic acid.

Potassium hydrogen saccharate was therefore dissolved in water, together with sufficient sulphuric acid to liberate free saccharic acid. The solution was then treated in exactly the same way as that employed in the oxidation of mucic acid. After concentrating the solution, extracting with alcohol, and concentrating the alcoholic extract, a syrup was obtained which showed the reactions characteristic of the syrup obtained in the same way from mucic acid.

The dihydrazone was prepared and purified under the same conditions as those adopted in the case of mucic acid. It was found to be an orange-yellow, microcrystalline substance, melting and decomposing at $242\text{--}244^\circ$ (quick heating). When mixed with about one-quarter of its weight of the dihydrazone obtained from mucic acid (m. p. 256°), the melting point was depressed to $239\text{--}241^\circ$:

0.1790 gave 23.45 c.c. N_2 at 14° and 764.5 mm. $\text{N} = 15.6$.

From these facts it would appear that the two dihydrazones have the same composition, but not identical configurations.

An ester was prepared from the dihydrazone in the same way as the ester of the dihydrazone derived from mucic acid. It consisted of bright orange-coloured needles, melting to a deep orange-red liquid at $164\text{--}165^\circ$ (quick heating). A mixture of the two dihydrazone esters melted at 156° .

The fact that the oxidation products of mucic and saccharic acids yield derivatives which are not identical is in agreement with the constitution for dihydroxymucic acid proposed above.

Note on Ethyl Hydrogen Mucate.

Fischer (*Ber.*, 1891, 24, 2142) states that an alcoholic solution of "paramucic acid," containing traces of metallic salts, deposits a crystalline substance "melting at about 175° ," which "from the analyses,

which gave no sharp figures, probably consists for the most part of the monoethyl ether of mucic acid."

The crystals deposited from the alcoholic extract after the oxidation of paramucic acid (p. 1251) gave as the mean of three not very concordant analyses: C = 39.15, H = 5.97 (ethyl hydrogen mucate requires C = 40.34, H = 5.88 per cent.), and melted at temperatures ranging between 175° and 181°. These facts are in agreement with Fischer's description of the substance supposed by him to be impure ethyl hydrogen mucate.

The substance has an acid reaction, is soluble in water or alcohol, but practically insoluble in ether. It reduces Fehling's solution on boiling, and gives a "silver mirror," in these respects resembling paramucic acid.

Titration with baryta gave the following result:

0.0200 of pure crystallised oxalic acid required 28.7 c.c. of the baryta solution. 0.0766 of the substance required 28.5 c.c.

Calculated for ethyl hydrogen mucate, 29.1 c.c.

The substance may therefore be regarded as identical with Fischer's impure ethyl hydrogen mucate.

I wish to express my sincere gratitude to Dr. Fenton for suggesting to me the above line of investigation, and for his valuable advice during its progress.

THE UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

CXLI.—*The Intramolecular Rearrangement of Diphenylamine ortho-Sulphoxides.*

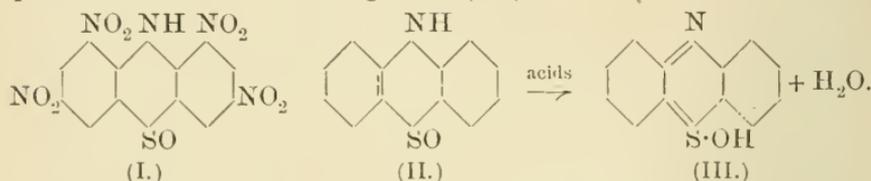
By EDWARD DE BARRY BARNETT and SAMUEL SMILES.

IN continuing the study of the derivatives of *S*-phenylphenazothionium, we desired to obtain a sulphoxide of diphenylamine which possesses stronger acidic properties than the dinitro-compounds previously employed, and for this purpose we undertook the preparation of the polynitro-derivatives of this group. The nitration of thio-diphenylamine has been studied by Bernthsen (*Annalen*, 1885, 230, 116), who, by carefully regulating the action of the nitric acid, isolated the di-*para*- and *isodinitro*-derivatives. We find that by conducting the nitration under more severe conditions, the tetra-nitro-sulphoxide is formed. In accordance with the facts previously

collected by Bernthsen (*loc. cit.*) from the dinitro-compounds, and by Störmer and Hoffmann (*Ber.*, 1898, **31**, 2535) from the nitration of diphenylamine, and also from the general rules governing the nitration of aromatic amines, the tetranitro-sulphoxide must have the constitution (I).

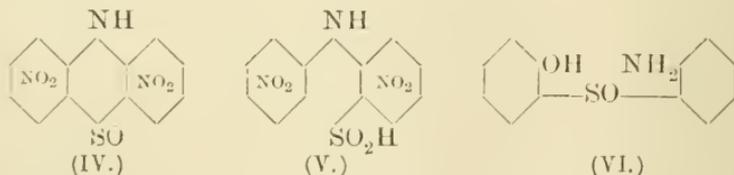
During the investigation of this substance it was observed that with certain reagents—such as a solution of hydrochloric acid in concentrated sulphuric acid—it is transformed into an isomeric compound, and, extending the inquiry to other sulphoxides of this series, we have found that the transformation is a general one.

It will be shown that the reaction consists essentially in the conversion of the imino-sulphoxide structure (II) into the ortho-quinonoid azothionium arrangement (III).



The reaction cannot be strictly termed an isomeric change, since under ordinary circumstances the azothionium products are found to contain a supplementary molecule of water, which as a rule does not occur in the sulphoxides. This molecule of water may, however, be removed, and the tetranitro-sulphoxide which contains the additional water yields an isomeric azothionium hydroxide.

On general considerations it might be considered possible that in this reaction fission of the thiazine ring (IV) takes place. If this were the case, the red substances obtained would have either the structure of a diphenylaminesulphinic acid (V) or that of an aminophenol sulphoxide (VI).



But apart from the improbability of this occurrence, these structures for the products of the reaction must be rejected, chiefly for the following reasons:

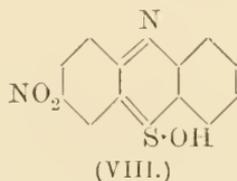
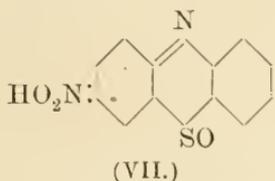
(i) It is difficult to imagine how substances of either of these types could lose water without producing the original sulphoxide.

(ii) The dinitro-products do not show the weakly acidic properties of the corresponding sulphoxides. They do not form sodium salts under the usual conditions with aqueous alkali hydroxide, whereas substances of either of these structures (V or VI) must do so.

(iii) The unsubstituted derivative obtained from diphenylamine ortho-sulphoxide is a base of moderate strength, since the salt is incompletely hydrolysed by boiling aqueous sodium carbonate. According to the latter of the given structures, the substance should be a weak base, and according to the former, an acid.

(iv) We have not been able to obtain benzoyl or alkyl derivatives of these substances.

The reaction was first studied with the previously-mentioned nitro-sulphoxides, and in these cases there are only two alternative structures for the isomeric products :



According to the first scheme they would be represented as para-quinonoid nitronic acids, and according to the second, as ortho-quinonoid sulphonium hydroxides.

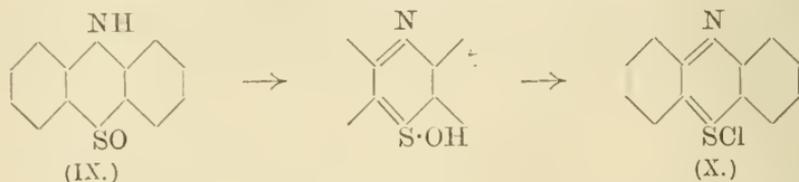
That the first alternative cannot be entertained is evident from the following considerations :

(i) The tetranitro-sulphoxide when treated with dilute aqueous sodium hydroxide is converted into a red sodium salt, which, according to the researches of Hantzsch and many others on similarly constituted compounds, must contain the para-quinonoid structure. By carefully treating the sodium salt with mineral acid, the red nitronic acid is liberated, but it is very unstable, and, during the process of isolation, changes into the original bright yellow sulphoxide. The product obtained from the tetranitro-sulphoxide by the action of hydrochloric acid cannot be the nitronic acid, for it is a quite stable substance, and, in fact, is formed when the sulphoxide is heated to about 180°.

(ii) In alcoholic solution with sodium ethoxide the tetranitro-, di-para-nitro-, and *isodinitro*-sulphoxides form red solutions of the nitronic salts. If the red isomeric forms of these sulphoxides had the nitronic structure, they should yield the same salts under these conditions ; but they do not, their salts being green or blue in alcoholic solution.

(iii) The dinitro-compounds do not form salts with dilute aqueous sodium hydroxide, and are thus of weaker acid character than the sulphoxide forms, which yield salts under these conditions. It has previously been shown (Smiles and Hilditch, *Trans.*, 1908, 93, 149) that the entrance of nitro-groups into the benzene nucleus of thiodiphenylamine weakens the basic properties of the quadrivalent

sulphur in the derivatives of *S*-phenylphenazothionium. Moreover, Kehrman (*Ber.*, 1906, 39, 914) has observed a similar relation in the ortho-quinonoid derivatives of phenazothionium. If this intramolecular rearrangement does not involve the nitro-groups, but merely concerns the thionyl and imino-groups of these sulphoxides, it follows that the unsubstituted diphenylamine sulphoxide (IX) should undergo the same change; moreover, the nitro-groups



being removed, the sulphonium base should be of stronger character and should furnish more stable salts (X). This is actually the case. Diphenylamine ortho-sulphoxide is formed by the interaction of hydrogen dioxide and thiodiphenylamine. The constitution of the product of this reaction might be considered doubtful, since Dunstan and Goulding (*Trans.*, 1899, 75, 792, 1004) have shown that hydrogen dioxide converts the secondary aliphatic amines into di- β -alkylhydroxylamines, but ample proof that the substance is a sulphoxide and does not contain the alternative hydroxylamine structure is afforded by the facts: (i) that under the same conditions diphenylamine is not attacked by hydrogen dioxide; (ii) that the substance does not show the strong reducing properties to be expected of a hydroxylamine derivative; and (iii) that hydrogen dioxide converts the aromatic sulphides into sulphoxides (Gazdar and Smiles, *Trans.*, 1908, 93, 1833).

When this sulphoxide is submitted to the action of aqueous hydrochloric acid it is at once converted into phenazothionium chloride, thus giving final proof that the products of this reaction possess the azothionium structure. It may be observed that Kehrman (*Ber.*, 1901, 34, 4170) has already obtained the chloride and other salts of phenazothionium by the acid oxidation of thiodiphenylamine.

From a comparison of the formulæ of the sulphoxides with those of the corresponding sulphonium bases, it would seem that this intramolecular change merely consists of the migration of hydrogen from the imino-group to the oxygen of the thionyl group. We have found reason for believing that this is not the true explanation of the reaction, but that the latter instead takes place by migration of hydroxyl from the quadrivalent sulphur to trivalent nitrogen. Since, however, our experiments are not yet complete, we reserve the discussion of this question for a future occasion. At present it is

sufficient to observe that, to be satisfactory, any theory of the mechanism must account for the following facts :

(i) The reaction proceeds more easily the stronger the basic character of the quadrivalent sulphur.

(ii) At least with the unsubstituted sulphoxide, the change is favoured by increasing the concentration and strength of the acid.

(iii) The anomalous behaviour of the tetranitro-sulphoxide, which, although the most difficult of the series to convert with acid reagents, is the only one transformed by the action of heat.

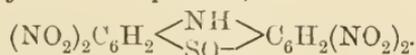
(iv) The absorption of the elements of water during the reaction.

It is our intention to extend the study of this reaction to aromatic hydroxy- and amino-sulphoxides and sulphonium bases.

EXPERIMENTAL.

Tetranitro-derivatives.

Tetranitrodiphenylamine Sulphoxide,



—Thiodiphenylamine is heated in an open vessel for about two hours with an excess of fuming nitric acid (D 1.5), and the solution is then poured into an excess of water and washed until the acid is completely removed. It is difficult exactly to define the conditions necessary to obtain a pure product. If the action be allowed to proceed too far, the liquid will be found to contain sulphuric acid, and the product must then be treated with acetone to remove the polynitro-derivatives of diphenylamine which are formed. If, however, the reaction be stopped at a suitable point before sulphuric acid appears in the solution, the product is almost pure and the yield quantitative. A sample was prepared for analysis by crystallisation from nitrobenzene, and it was thus obtained in minute, lemon-yellow crystals :

0.0966 gave 0.1285 CO_2 and 0.0219 H_2O . C = 36.27 ; H = 2.5.

0.1984 ,, 0.2671 CO_2 ,, 0.0378 H_2O . C = 36.71 ; H = 2.1.

0.4278 ,, 0.2484 BaSO_4 . S = 7.97.

$\text{C}_{12}\text{H}_5\text{O}_9\text{N}_5\text{S}$ requires C = 36.54 ; H = 1.27 ; S = 8.10 per cent.

When recrystallised from *p*-tolyl methyl ether the substance separates in long needles which contain the solvent, but the latter may be removed by washing with alcohol or ether, when the crystals break up into a fine powder. Probably these crystals contain two molecular proportions of the phenolic ether, but the correct amount is difficult to determine, since it is very loosely combined. Two samples were analysed.

(1) Dried in a vacuum :

0.0843 gave 0.1500 CO_2 and 0.0306 H_2O . $\text{C} = 48.53$; $\text{H} = 4.03$.

(2) Dried in air at atmospheric temperature and pressure :

0.1391 gave 0.2572 CO_2 and 0.0562 H_2O . $\text{C} = 50.42$; $\text{H} = 4.49$.

$\text{C}_{12}\text{H}_5\text{O}_9\text{N}_5\text{S}, \text{C}_8\text{H}_{10}\text{O}$ requires $\text{C} = 46.4$ per cent.

$\text{C}_{12}\text{H}_5\text{O}_9\text{N}_5\text{S}, (\text{C}_8\text{H}_{10}\text{O})_2$,, $\text{C} = 56.3$,,

The product obtained by the correct nitration of thiodiphenylamine, and without further purification with high boiling solvents, is the pure sulphoxide, but it now contains an additional molecule of water. A sample which had been dried in the steam-oven was analysed :

0.1041 gave 0.1331 CO_2 and 0.0162 H_2O . $\text{C} = 34.87$; $\text{H} = 1.73$.

0.4462 ,, 0.2540 BaSO_4 . $\text{S} = 7.88$.

0.1876 ,, 27.8 c.c. N_2 at 20° and 744 mm. $\text{N} = 16.90$.

$\text{C}_{12}\text{H}_5\text{O}_9\text{N}_5\text{S}, \text{H}_2\text{O}$ requires $\text{C} = 34.81$; $\text{H} = 1.69$; $\text{S} = 7.75$; $\text{N} = 16.95$ per cent.

When this substance is heated to 180 — 200° , only a slight loss in weight occurs, but the greater portion of the sulphoxide is transformed into the sulphonium hydroxide. That this hydrated sulphoxide is not the sulphone, which differs from it only slightly in elemental composition, is proved by the fact that it may be reduced to diaminothionine, and it appears from the work of Berntsen (*Ber.*, 1906, **39**, 1807) that the nitrosulphones of this series are not thus converted into thionine derivatives. Moreover, it will be later shown that the substance may be condensed with phenetole, yielding the salt of the *S*-phenetyl derivative, and this reaction shows the presence of the thionyl grouping.

Tetra-nitrodiphenylamine ortho-sulphoxide does not melt below 250° and it is very sparingly soluble in the usual organic media of low boiling point.

Sodium Salt.—This sulphoxide behaves as a weak acid, and with aqueous sodium hydroxide furnishes a scarlet sodium salt. When boiled with this reagent some decomposition takes place, one or more nitro-groups being displaced, but when triturated with a warm aqueous solution of the alkali hydroxide a red, flocculent precipitate is deposited. Estimation of sodium in two different samples showed that it is probably an acid salt :

0.3533 gave 0.0269 Na_2SO_4 . $\text{Na} = 2.47$.

0.4160 ,, 0.0369 Na_2SO_4 . $\text{Na} = 2.87$.

$\text{C}_{12}\text{H}_4\text{O}_9\text{N}_5\text{SNa}, \text{C}_{12}\text{H}_5\text{O}_9\text{N}_5\text{S}$ requires $\text{Na} = 2.85$ per cent.

It seems to be very readily decomposed into its components by treatment with cold acetone, which dissolves the normal sodium salt, leaving the sparingly soluble yellow acid.

A sample of the sodium salt obtained in this manner was analysed :

0.4160 gave 0.0503 Na_2SO_4 . $\text{Na} = 4.36$.

$\text{C}_{12}\text{H}_4\text{O}_9\text{N}_5\text{SNa}$ requires $\text{Na} = 5.52$ per cent.

The addition of dilute mineral acids to the aqueous solution of the sodium salt furnishes a precipitate of a red form of the sulphoxide. A sample of this substance was collected and washed with cold water until free from excess of acid, but on being dried in the steam-oven for analysis it rapidly changed colour, and finally became orange-coloured :

0.1010 gave 0.1287 CO_2 and 0.0187 H_2O . $\text{C} = 34.75$; $\text{H} = 2.10$.

$\text{C}_{12}\text{H}_5\text{O}_9\text{N}_5\text{S}$ requires $\text{C} = 34.81$; $\text{H} = 1.69$ per cent.

Diaminotionine.—Tetranitrodiphenylamine ortho-sulphoxide was mixed with alcohol and reduced with tin and hydrochloric acid in the usual manner. The colourless solution was mixed with excess of aqueous ferric chloride, and finally the precipitation of the dye was completed by the addition of salt solution. The precipitate was collected and treated with concentrated hydrochloric acid, which dissolved the amino-derivative, leaving the insoluble residue of inorganic matter. The dye-stuff was obtained in deep blue scales by mixing the hydrochloric acid solution with water and keeping the mixture for some days at the atmospheric temperature. Several unsuccessful attempts were made to remove by physical means the excess of hydrochloric acid contained in this substance, but analysis showed that the content of carbon was too low, and that of halogen too high, for the monochloride, and these did not correspond with any definite formula. However, it seems that treatment with dilute aqueous sodium carbonate removes the excess of acid, since it was found that

0.1006 gave 0.1615 CO_2 and 0.0354 H_2O . $\text{C} = 43.7$; $\text{H} = 3.9$.

$\text{C}_{12}\text{H}_{12}\text{N}_5\text{ClS}, 2\text{H}_2\text{O}$ requires $\text{C} = 43.76$; $\text{H} = 4.25$ per cent.

but further analysis of the substance was not made.

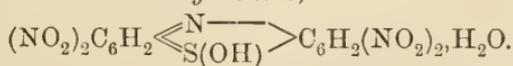
Diaminotionine chloride is soluble in hot water or alcohol. In the latter solvent it exhibits a red fluorescence.

The *platinichloride* was obtained as a brown, crystalline powder by adding aqueous chloroplatinic acid to a solution of the chloride :

0.3351 gave 0.0732 Pt. $\text{Pt} = 21.55$.

$\text{C}_{24}\text{H}_{24}\text{N}_{10}\text{Cl}_6\text{S}_2\text{Pt}$ requires $\text{Pt} = 21.10$ per cent.

Tetranitrophenazothionium hydroxide,



—The following methods of preparation were carried out with the

hydrated form of the sulphoxide, the analysis of which is described on a former page.

(a) *With Hydrochloric Acid in Sulphuric Acid Solution.*—Unlike the other sulphoxides of this series, the tetranitro-derivative dissolves in concentrated sulphuric acid without intense colour; the solution is a greenish-yellow colour. The addition of hydrochloric acid to this solution causes the appearance of a bright red colour, and the reaction is a very delicate one. The same effect is produced by phenetole and similar compounds, and it will be shown later that with these reagents the *S*-phenyl derivatives of the series are formed. It may be remarked that with thiophen the reaction is so delicate that it may be used as a test for the presence of this substance in benzene.

A mixture of excess of concentrated sulphuric acid with tetranitrothiodiphenylamine ortho-sulphoxide was saturated at atmospheric temperature with hydrogen chloride. The passage of the gas was continued for about twenty-four hours, and the mixture was continually stirred. When the yellow particles of the sulphoxide seemed to have completely disappeared, the deep red solution was filtered through glass wool and then slowly poured on to pounded ice. The precipitate was collected and washed until the sulphuric and hydrochloric acids were completely removed. After purification the substance contained no halogen:

0.1926 gave 0.2594 CO₂ and 0.0392 H₂O. C = 36.73; H = 2.26.

0.1974 ,, 0.1007 BaSO₄. S = 7.70.

C₁₂H₅O₉N₅S requires C = 36.46; H = 1.27; S = 8.09 per cent.

It may be observed that the transformation does not take place with sulphuric acid alone, and this distinguishes the tetranitro- from the other derivatives which are readily converted by this reagent.

(b) *With an Alcoholic Solution of Hydrochloric Acid.*—The tetranitro-sulphoxide was mixed with a solution of hydrogen chloride in absolute alcohol which had been saturated with the gas at the atmospheric temperature. A portion of the sulphoxide at once dissolved, giving a deep red solution. The reaction was allowed to continue (1) by keeping the mixture at the laboratory temperature for twenty-six days, or (2) by heating the mixture in a sealed tube to 150° for five hours. In the latter case, when the cold tube had been opened and the excess of ethyl chloride had been allowed to evaporate, the thionium hydroxide was obtained in large, blunt, bright red prisms. After purification, the products from the two sources were dried at 100° and analysed:

(I) 0.1045 gave 0.1337 CO₂ and 0.0194 H₂O. C = 34.89; H = 2.07.

(II) 0.1033 ,, 0.1316 CO₂ ,, 0.0205 H₂O. C = 34.84; H = 1.81.

C₁₂H₅O₉N₅S requires C = 34.81; H = 1.69 per cent.

Tetranitrophenazothionium hydroxide does not melt below 250°. It is insoluble in water and very sparingly soluble in the usual organic

solvents, but it is rather more soluble in acetone, giving a red solution from which it is deposited on spontaneous evaporation in red needles. Tetranitrophenazothionium hydroxide may also be obtained by heating the sulphoxide to 180—200° for a few hours. No appreciable loss of weight takes place, and the product is dark red in colour, and furnishes the green colour with alcoholic alkali hydroxide which is characteristic of the azothionium form.

Sodium Salt.—When triturated at the ordinary temperature with 10 per cent. aqueous alkali hydroxide, tetranitrophenazothionium hydroxide forms a sticky, green mass, which is converted by cold water into a red sodium salt. This could not be obtained sufficiently pure for analysis. The alcoholic solution of this tetranitro-derivative gives a green colour with sodium ethoxide.

Oxidation.—Tetranitrophenazothionium hydroxide is readily attacked by concentrated nitric acid, and is thereby oxidised to the sulphone. After purification, the product of this reaction was analysed :

0.1004 gave 0.1292 CO₂ and 0.0250 H₂O. C = 35.05 ; H = 2.76.

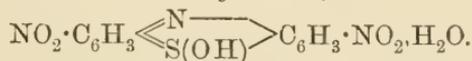
C₁₂H₅O₁₀N₅S requires C = 35.04 ; H = 1.22 per cent.

That the substance is not the hydrated form of the sulphoxide is shown by the action of alkali hydroxide, which furnishes a well-defined crystalline salt, and by the very weak red coloration produced by adding hydrochloric acid to the sulphuric acid solution of the substance. The weak colour produced is no doubt due to the presence of traces of the sulphoxide in the azothionium hydroxide.

Dinitro-derivatives.

The dinitrodiphenylamine sulphoxides employed were those previously obtained by Bernthsen (*loc. cit.*) by the regulated action of nitric acid on thiodiphenylamine. These substances are far more readily converted into the azothionium compounds than the tetranitro-compounds described in the previous pages ; in fact, the rearrangement can be effected by sulphuric acid or alcoholic hydrochloric acid in a few hours at the laboratory temperature.

3 : 9-Dinitrophenazothionium Hydroxide,



! Di-*p*-nitrophenylamine sulphoxide was treated in the three following ways :

(a) *Concentrated Sulphuric Acid.*—The rearrangement of the sulphoxide to the azothionium form takes place only slowly with this reagent, and it is difficult to obtain a pure product, since the azothionium hydroxide is decomposed by the acid before the sulphoxide has been completely transformed. In one experiment the brown

solution of the sulphoxide in sulphuric acid was kept for one hour and then poured into water. After being purified and dried, a sample was analysed:

0.1011 gave 0.1745 CO_2 and 0.0269 H_2O . $\text{C} = 47.07$; $\text{H} = 2.9$.

$\text{C}_{12}\text{H}_7\text{O}_5\text{N}_3\text{S}$ requires $\text{C} = 47.2$; $\text{H} = 2.3$ per cent.

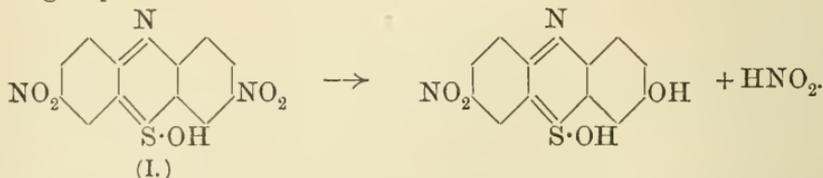
The product was evidently a mixture of the sulphoxide and the sulphonium form, since it was pale brown in colour and did not give the pure green with alcoholic alkali hydroxide.

In another experiment the solution of the sulphoxide in concentrated sulphuric acid was kept for a longer time. After sixteen hours the solution had become green, and had a strong odour of oxides of nitrogen. The precipitate now formed by pouring into cold water was collected, and, after thorough washing, was extracted with cold dilute sodium hydroxide solution, in which the greater part dissolved. The alkaline solution was acidified, and the precipitate was collected, dried, and recrystallised from nitrobenzene. The treatment with aqueous sodium hydroxide was repeated. An analysis of a purified sample gave the following result:

0.1856 gave 0.3292 CO_2 and 0.0646 H_2O . $\text{C} = 48.4$; $\text{H} = 3.8$.

$\text{C}_{12}\text{H}_{10}\text{O}_5\text{N}_2\text{S}$ requires $\text{C} = 48.9$; $\text{H} = 3.4$ per cent.

These data show that the dinitrophenazothionium hydroxide (I) at first produced is acted on by the excess of sulphuric acid, nitrous acid being liberated and hydroxyl being introduced in place of the nitro-group.



3-Nitro-9-hydroxyphenazothionium hydroxide forms minute, reddish-brown crystals, which are insoluble in water and alcohol. The solutions in aqueous sodium hydroxide are reddish-violet.

(b) *With Hydrochloric Acid in Sulphuric Acid Solution.*—The process employed was similar to that described under the tetranitro-derivative; but here the reaction was complete in about four hours. As obtained by this method, the product was isomeric with the original sulphoxide, and it did not contain halogen:

0.1000 gave 0.1725 CO_2 and 0.0264 H_2O . $\text{C} = 47.04$; $\text{H} = 2.9$.

0.2655 „ 0.2084 BaSO_4 . $\text{S} = 10.76$.

$\text{C}_{12}\text{H}_7\text{O}_5\text{N}_3\text{S}$ requires $\text{C} = 47.2$; $\text{H} = 2.3$; $\text{S} = 10.49$ per cent.

Analysis of the sample of sulphoxide employed in this reaction gave $\text{C} = 47.2$ per cent.

(c) *With Alcoholic Hydrochloric Acid.*—The finely powdered sulphoxide was shaken with this reagent for four or five hours at the laboratory temperature. If the quantity of the reagent taken be sufficient to dissolve the sulphoxide, the transformation can be more rapidly effected, since then the azothionium hydroxide crystallises from the solution in about one hour or even less. In either case the crystalline mass was separated from the mother liquor, and washed with alcohol and finally, with water. The product did not contain ionisable halogen, but it was observed that if the action of the halogen acid was prolonged, or if the temperature was allowed to rise above the ordinary limits, traces of halogens may be present in other forms of combination. This impurity seems to consist of a colourless substance, which we have isolated but not yet fully examined. The crude product was crystallised from nitrobenzene or from aniline:

0.1502 gave 0.2432 CO_2 and 0.0396 H_2O . C = 44.16 ; H = 2.93.

0.0967 „ 10.8 c.c. N_2 at 13° and 767 mm. N = 13.25.

$\text{C}_{12}\text{H}_7\text{O}_5\text{N}_3\text{S}\cdot\text{H}_2\text{O}$ requires C = 44.58 ; H = 2.8 ; N = 13.0 per cent.

The supplementary molecule of water present in the substance prepared in this manner cannot be removed at 100°, and attempts to displace it at higher temperatures were unsatisfactory, since some decomposition seemed to take place.

3 : 9-Dinitrophenazothionium hydroxide is insoluble in water, alcohol, or ether, slightly soluble in hot glacial acetic acid, and easily so in hot aniline or nitrobenzene. It forms chocolate-brown needles, which melt and decompose at about 240°. Solutions in concentrated sulphuric acid are deep green in colour.

Sodium Salts.—The azothionium hydroxide does not form salts with cold aqueous alkali hydroxide, and it is apparently decomposed by the boiling reagent. With alcoholic alkali hydroxide it yields an intense green coloration. This behaviour sharply distinguishes the substance from the corresponding sulphoxide. The latter is sparingly attacked by cold aqueous alkali, giving bright red solutions of the sodium salt, and it is readily soluble in the alcoholic reagent, producing the same colour. When the sulphoxide is warmed with aqueous sodium hydroxide, the sodium salt is readily obtained in well defined, glistening scales. Two recrystallised specimens of this salt were dried in the steam-oven and analysed :

(a) 0.2198 gave 0.0310 Na_2SO_4 . Na = 4.59.

0.2181 „ 0.1560 BaSO_4 . S = 9.81.

(b) 0.2844 „ 0.0381 Na_2SO_4 . Na = 4.34.

$\text{C}_{12}\text{H}_7\text{O}_5\text{N}_3\text{S}\cdot 2\text{C}_{12}\text{H}_6\text{O}_5\text{N}_3\text{SNa}$ requires Na = 4.79 ; S = 10.0 per cent.

Reduction of the dinitroazothionium hydroxide with zinc dust and

hydrochloric acid, and subsequent oxidation of the leuco-base with ferric chloride, furnishes thionine.

Oxidation with chromic acid in glacial acetic acid solution yields a bright yellow, crystalline substance, which is soluble in hot nitrobenzene and does not melt below 250°:

0.1047 gave 0.1642 CO₂ and 0.0264 H₂O. C = 42.76; H = 2.8.

C₁₂H₇O₆N₃S, H₂O requires C = 42.48 and H = 2.65 per cent.

This substance is therefore probably the sulphone, but we have been unable to prove that fission of the thiazine ring has not taken place.

isoDinitrophenazothionium Hydroxide, NO₂·C₆H₃ $\begin{matrix} \text{N} \\ \text{---} \\ \text{S}(\text{OH}) \end{matrix}$ C₆H₃·NO₂.

—This was prepared from *isodinitrodiphenylamine sulphoxide* by the action of alcoholic hydrogen chloride, the procedure being the same as that previously described for the other nitro-derivatives. The transformation is effected in about the same time as that of the di-*p*-nitro-sulphoxide. The product which crystallised from the acid mother liquor was thoroughly washed with alcohol and water, and if care be taken to regulate the action of the halogen acid, the substance thus obtained is quite free from halogen, and consists of the pure hydrated form of the thionium derivative. A sample which had been dried at 100° was analysed:

0.1000 gave 0.1622 CO₂ and 0.0255 H₂O. C = 44.24; H = 2.83.

0.2551 ,, 0.1854 BaSO₄. S = 9.96.

C₁₂H₇O₅N₃S, H₂O requires C = 44.58; H = 2.8; S = 9.91 per cent.

When the substance was crystallised from aniline, it was obtained in the anhydrous form:

0.1002 gave 0.1749 CO₂ and 0.0242 H₂O. C = 47.60; H = 2.6.

0.1596 ,, 19.2 c.c. N₂ at 12° and 744.6 mm. N = 13.93.

C₁₂H₇O₅N₃S requires C = 47.2; H = 2.3; N = 13.77 per cent.

isoDinitrophenazothionium hydroxide is insoluble in cold alcohol or water, and readily soluble in hot aniline or nitrobenzene. It forms chocolate-coloured needles, which melt and decompose at 199°. In its chemical behaviour the substance closely resembles the di-*p*-nitro-compound. It does not yield an alkali salt with cold aqueous sodium hydroxide, but the alcoholic solution when mixed with sodium hydroxide develops a deep blue colour. It is readily soluble in concentrated sulphuric acid, the solution being reddish-brown in colour.

Reduction and oxidation furnish similar products to those obtained from the di-*p*-nitro-compound.

Unsubstituted Derivatives.

Diphenylamine ortho-Sulphoxide, $C_6H_4 \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ \text{SO} \end{array} C_6H_4$.—A solution of 5 grams of thiodiphenylamine in about 150 c.c. of acetone was rendered alkaline with a few drops of sodium ethoxide solution. Three grams of a 30 per cent. solution of hydrogen dioxide were then added, more acetone being added if necessary to retain the diphenylamine in solution. The mixture was then kept at the atmospheric temperature. The sulphoxide was gradually deposited in large, prismatic needles, which at the end of ten days were collected, 3 grams being obtained. Diphenylamine ortho-sulphoxide obtained in this manner is almost pure, but it may be recrystallised from acetone, in which it is sparingly soluble :

0.1023 gave 0.2501 CO_2 and 0.0411 H_2O . C = 66.68 ; H = 4.4.

$C_{12}H_9ONS$ requires C = 66.98 ; H = 4.16 per cent.

The substance melts with profound decomposition at about 250°.

This unsubstituted sulphoxide is converted into the azothionium base more easily than any of the others here described. The change is instantaneously effected by aqueous mineral acids, and slowly by hot glacial acetic acid. With concentrated sulphuric acid it gives a green solution, which turns red on dilution with water.

Phenazothionium Chloride, $C_6H_4 \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{SCl} \end{array} C_6H_4, H_2O$.—Diphenylamine ortho-sulphoxide, in quantities of about 1 gram at a time, was shaken with a freshly prepared solution (15 c.c.) of hydrogen chloride in dry alcohol. Care was taken not to allow the temperature to rise above the ordinary limits. The sulphoxide at once dissolved, the liquid assuming an intense reddish-brown colour, and in about ten minutes phenazothionium chloride crystallised from the mother liquor in dark brown needles. These were collected, and, after being washed with alcohol, were dried for analysis to constant weight in a vacuum over solid alkali hydroxide :

0.1013 gave 0.2130 CO_2 and 0.0331 H_2O . C = 57.34 ; H = 3.63.

When this sample had remained for two days longer under diminished pressure it was again analysed :

0.1592 gave 0.3338 CO_2 and 0.0572 H_2O . C = 57.19 ; H = 3.99.

$C_{12}H_8NClS, H_2O$ requires C = 57.22 ; H = 3.98 per cent.

When heated at 100° for a short time, this substance is transformed into a green compound, which is apparently also formed by diluting the aqueous solution. Alkali hydroxide precipitates this green substance from an aqueous solution of the chloride. Phenazo-

thionium chloride contains ionisable chlorine, but the salt is not completely hydrolysed by boiling aqueous sodium carbonate solution. Other salts of this and similar bases have been previously described by Kehrmann (*Ber.*, 1901, **34**, 4170), who obtained them by the acid oxidation of thiodiphenylamine derivatives.

The investigation of this rearrangement is being continued with the object of determining the mechanism of the reaction.

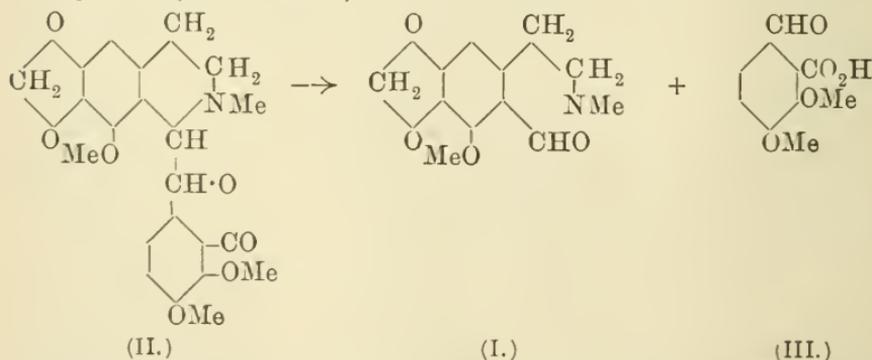
In conclusion, we desire to express our thanks to the Research Fund Committee of the Chemical Society for a grant which has defrayed the expense of this research.

THE ORGANIC CHEMISTRY LABORATORY,
UNIVERSITY COLLEGE,
LONDON.

CXLII.—isoQuinoline Derivatives. Part I. Oxidation of Laudanosine.

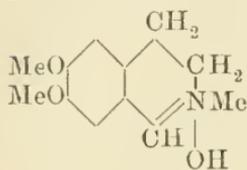
By FRANK LEE PYMAN.

THE alkaloids cotarnine (I) and hydrastinine are particularly interesting, not only on account of their therapeutic value, but also by reason of their chemical properties, for they are at the same time secondary amines and benzaldehydes, and form salts derived from 3:4-dihydroisoquinolinium hydroxide. They have hitherto been the only known members of the class they represent, and are produced by the oxidation of the similarly constituted alkaloids narcotine (II) and hydrastine respectively together with opianic acid (III) according to the equation (for cotarnine):

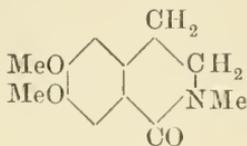


Cotarnine and hydrastinine may also be prepared by the oxidation of their reduction products, hydrocotarnine and hydrohydrastinine re-

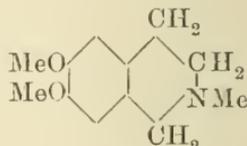
and hydrastinine; it is a colourless, crystalline solid, forming primrose coloured salts of 6:7-dimethoxy-2-methyl-3:4-dihydroisoquinolinium hydroxide (IX) by substitution; when boiled with aqueous sodium hydroxide, it undergoes Cannizzaro's reaction, yielding the anhydrides of the corresponding acid and alcohol, 1-keto-6:7-dimethoxy-2-methyl-tetrahydroisoquinoline (X) and 6:7-dimethoxy-2-methyltetrahydroisoquinoline (XI) respectively.



(IX.)



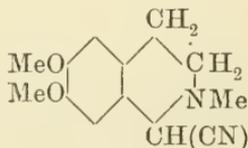
(X.)



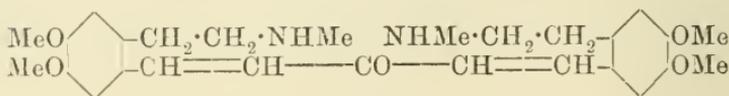
(XI.)

Aqueous solutions of its salts yield with aqueous potassium cyanide a colourless, crystalline compound, 1-cyano-6:7-dimethoxy-2-methyl-tetrahydroisoquinoline (XII), analogous to cyanocotarnine (Freund, *Ber.*, 1900, **33**, 386).

The base forms a condensation product with acetone,* *bis*(4:5-dimethoxy-2- β -methylaminoethylbenzylidene)-acetone (XIII), which differs from the condensation products of cotarnine and hydrastinine with acetone (Liebermann and Kropf, *Ber.*, 1904, **37**, 211) in that two molecules of the base take part in it.



(XII.)

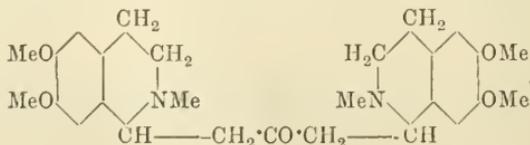


(XIII.)

Bis-(4:5-dimethoxy-2- β -methylaminoethylbenzylidene)-acetone forms a neutral dihydrochloride, which is decomposed by boiling water with the formation of 6:7-dimethoxy-2-methyl-3:4-dihydroisoquinolinium chloride; on examination, anhydrocotarnineacetone hydrochloride was found to undergo a similar decomposition.

During the oxidation of laudanosine a considerable quantity of

* It is equally possible that this condensation product has the constitution represented by the following formula (compare Liebermann and Kropf, *loc. cit.*):



brown, granular matter separates from the solution, and there was obtained from this a small quantity of a saturated compound, $C_{14}H_8(OMe)_4$. This substance is derived from a hydrocarbon, $C_{14}H_{12}$, and its formation may possibly be due to the decomposition of veratryl alcohol in a manner somewhat similar to the formation of a hydrocarbon, $C_{14}H_{12}$, from benzyl alcohol (Cannizzaro, *Annalen*, 1854, 92, 14) or benzyl ethyl ether (Schickler, *J. pr. Chem.*, 1896, [ii], 53, 369).

The investigation of the products of the oxidation of laudanosine and other 1-benzyl-2-alkyltetrahydroisoquinolines is being continued.

EXPERIMENTAL.

Oxidation of Laudanosine.

Eighty grams of laudanosine were dissolved in a mixture of 160 grams of sulphuric acid and 1.2 litres of water, and mechanically stirred with 48 grams of pyrolusite containing 80 per cent. of manganese dioxide for three-quarters of an hour on a steam-bath. The solution gradually became brown and turbid, and eventually deposited a brown solid. After cooling, the solution was filtered from the solid matter (*A*) and extracted with benzene, which removed the soluble non-basic constituent (*B*). The solution was next rendered alkaline with sodium carbonate, filtered from the precipitated manganese carbonate, and extracted with benzene; this removed about 1 gram of yellow oil, which has not yet been fully investigated. The liquor was rendered strongly alkaline with sodium hydroxide, and again completely extracted with benzene. The latter was then filtered, and extracted with successive small quantities of dilute hydrochloric acid so long as the latter became neutralised; these extracts were combined, rendered faintly acid by the addition of hydrochloric acid, and evaporated to a thick, brown syrup; on stirring this with dry acetone, 6:7-dimethoxy-2-methyl-3:4-dihydroisoquinolinium chloride separated as a yellow, crystalline powder, which was collected and washed with acetone; it amounted to 40 grams. The acetone mother liquors gave a further quantity of 3 grams of the same compound. The total yield, 43 grams, represents 63 per cent. of the theoretical.

Isolation of a Compound, $C_{14}H_8(OMe)_4 \cdot \frac{1}{2}H_2O$, from the Brown Solid "A."

The amount of air-dried, brown, granular solid was 28 grams. This was combined with the product from another similar experiment and worked up as follows:

Forty-six grams were extracted with ether in a Soxhlet apparatus for five hours. The ether removed 7 grams of reddish-black, resinous

matter, and deposited also 0.95 gram of a mixture of crystals and tarry matter. The residue was then extracted with alcohol in a Soxhlet apparatus for six hours, and the residue concentrated to about 100 c.c., when 2 grams of pale brown crystals were deposited. Further concentration of the alcohol yielded only brown, amorphous compounds, which were not further investigated. The crystals obtained from the alcohol were recrystallised from acetone, and formed large, oblong, rectangular, colourless plates, which melted at 231° (corr.). A further quantity of this substance was obtained from the solids deposited by the ethereal extract :

0.2741, air-dried, lost 0.0085 at 100° . $H_2O = 3.1$.

$C_{14}H_8(OMe)_4 \cdot \frac{1}{2}H_2O$ requires $H_2O = 2.9$ per cent.

0.1344, dried at 100° , gave 0.3535 CO_2 and 0.0806 H_2O . $C = 71.7$;
 $H = 6.7$.

0.2520, dried at 100° , gave 0.7901 AgI. $OMe = 41.4$.

$C_{14}H_8(OMe)_4$ requires $C = 71.9$; $H = 6.7$; $OMe = 41.3$ per cent.

The molecular weight of this compound was very kindly determined by Dr. Barger by his microscopic method (Trans., 1904, 85, 286). A solution containing 0.0682 gram of the compound, dried at 100° , in 1.120 grams of chloroform was intermediate between 0.18 and 0.20 mol. of azobenzene as standard, whence M.W. = 338—305, mean 321.

$C_{14}H_8(OMe)_4$ requires M.W. = 300.

The compound is easily soluble in acetone, chloroform, or pyridine, fairly readily so in alcohol, but very sparingly soluble in water or the other usual organic solvents. A chloroform solution of the compound did not decolorise bromine, nor did an acetone solution immediately decolorise aqueous permanganate.

Identification of Veratraldehyde.

The non-basic constituent (*B*) removed from the acid liquor by benzene was obtained after the removal of the solvent as a dark brown oil with an odour similar to that of vanillin. On fractionation under 53 mm. pressure, the temperature rose quickly to 195° , and more than 5 grams distilled at 198 — 201° (corr.). On refractionation under normal pressure, it distilled at 278 — 282° , mainly, however, at 281° (corr.). It solidified on cooling, and melted at 42 — 43° (corr.) :

0.1587 gave 0.3796 CO_2 and 0.0864 H_2O . $C = 65.2$; $H = 6.1$.

$C_9H_{10}O_3$ requires $C = 65.0$; $H = 6.1$ per cent.

This substance is therefore veratraldehyde.

4 : 5-Dimethoxy-2- β -methylaminoethylbenzaldehyde (VIII, p. 1267).

This base is obtained as an oil, which gradually becomes crystalline, on the addition of 50 per cent. aqueous sodium hydroxide to the con-

concentrated aqueous solution of its hydrochloride. It crystallises from acetone in prismatic needles, which melt at 123—124° (corr.), and is sparingly soluble in water, giving a solution which is strongly alkaline to litmus. The base is precipitated from a concentrated aqueous solution on the addition of concentrated aqueous sodium hydroxide; it is easily soluble in alcohol or chloroform, but sparingly so in the other usual organic solvents. The base decomposes when heated for an hour at 100°, giving an odour similar to that of methylamine:

0.1530, air-dried, gave 0.3620 CO₂ and 0.1038 H₂O. C = 64.5; H = 7.6.

0.1608 " " 8.8 c.c. N₂ at 17° and 734 mm. N = 6.1.

C₁₂H₁₇O₃N requires C = 64.5; H = 7.7; N = 6.3 per cent.

4:5-Dimethoxy-2-β-methylaminoethylbenzaldehyde combines with acids, forming salts by substitution of the isomeric 6:7-dimethoxy-2-methyl-3:4-dihydroisoquinolinium hydroxide (IX, p. 1268).

The *chloride* crystallises from aqueous solution in a mass of primrose needles, which contain three and a-half molecular proportions of water of crystallisation, and melt at 61—62° (corr.) to an opaque liquid. When dried at 100°, this salt melts and decomposes at 186° (corr.). It is very easily soluble in water or alcohol, giving yellow solutions, which are neutral to litmus, and show a blue fluorescence when diluted; it is sparingly soluble in chloroform, and very sparingly so in the other usual organic solvents:

0.1510, air-dried, gave 0.2629 CO₂ and 0.1034 H₂O. C = 47.5; H = 7.7.

0.3139 " " 0.4710 AgI. OMe = 19.8.

0.1116 " " lost 0.0232 at 100°. H₂O = 20.8.

C₁₀H₁₀(OMe)₂NCl, 3½H₂O requires C = 47.3; H = 7.6; OMe = 20.4; H₂O = 20.7 per cent.

0.1429, dried at 100°, gave 0.3115 CO₂ and 0.0849 H₂O. C = 59.5; H = 6.7.

0.1398, dried at 100°, gave 6.8 c.c. N₂ at 15° and 748 mm. N = 5.6.

0.2141 " " 0.1260 AgCl. Cl = 14.6

C₁₂H₁₆O₂NCl requires C = 59.6; H = 6.7; N = 5.8; Cl = 14.7 per cent.

The *bromide* crystallises from moist acetone in primrose needles, which contain two molecules of water of crystallisation, and sinter without entirely melting at 87—90° (corr.). On drying, the salt becomes lemon-yellow in colour, and melts at 195° (corr.). The properties of this salt are similar to those of the chloride:

0.2996, air-dried salt, lost 0.0328 at 110°. H₂O = 10.9.

C₁₂H₁₆O₂NBr, 2H₂O requires H₂O = 11.2 per cent.

0.1603, dried at 110°, gave 0.1067 AgBr. Br = 28.3.

C₁₂H₁₆O₂NBr requires Br = 27.9 per cent.

The *aurichloride* crystallises from alcohol in chestnut-brown, serrated needles, which melt at 169° (corr.). It is anhydrous, and is almost

insoluble in water or cold alcohol, but fairly easily soluble in hot alcohol:

0.1946 gave 0.0700 Au. Au = 36.0.

$C_{12}H_{16}O_2NCl_4Au$ requires Au = 36.2 per cent.

The *picrate* crystallises from alcohol in long, yellow, glistening needles, which melt at 169—170° (corr.).

1-Cyano-6 : 7-dimethoxy-2-methyltetrahydroisoquinoline (XII, p. 1268).

Ten grams of 6 : 7-dimethoxy-2-methyl-3 : 4-dihydroisoquinolinium chloride were dissolved in 50 c.c. of water, and mixed with a solution of 3 grams of potassium cyanide in 10 c.c. of water. A sticky, amorphous mass separated, which soon became hard and crystalline. The yield was 7.2 grams of nearly pure product, that is, 94 per cent. of the theoretical.

1-Cyano-6 : 7-dimethoxy-2-methyltetrahydroisoquinoline crystallises from moist ether in clusters of colourless, prismatic, glistening rods, which melt at 127—128° (corr.). It is insoluble in water, moderately easily so in absolute alcohol, but sparingly so in ether:

0.1522 gave 0.3750 CO₂ and 0.0964 H₂O. C = 67.2; H = 7.1.

$C_{13}H_{16}O_2N_2$ requires C = 67.2; H = 7.0 per cent.

Action of Hot Aqueous Sodium Hydroxide on 4 : 5-Dimethoxy-2-β-methylaminoethylbenzaldehyde. Formation of 1-Keto-6 : 7-dimethoxy-2-methyltetrahydroisoquinoline and 6 : 7-Dimethoxy-2-methyltetrahydroisoquinoline.

Eighteen grams of 4 : 5-dimethoxy-2-β-methylaminoethylbenzaldehyde were mixed with 600 c.c. of 5 per cent. aqueous sodium hydroxide, and boiled for six hours under a reflux condenser. The liquid was cooled, exactly neutralised with hydrochloric acid, evaporated to low bulk, and completely extracted with ether, which gave on distillation 7.5 grams of crude 1-keto-6 : 7-dimethoxy-2-methyltetrahydroisoquinoline, melting at 110—113°; the liquor was rendered alkaline with sodium carbonate, and again extracted with ether, which gave on distillation 8.0 grams of crude 6 : 7-dimethoxy-2-methyltetrahydroisoquinoline, melting at 60—80°; on then adding sodium hydroxide to the liquor and again completely extracting with ether, only a trace of dark resin was obtained.

1-Keto-6 : 7-dimethoxy-2-methyltetrahydroisoquinoline (X, p. 1268).

The crude product may be readily purified by recrystallisation from ether, from which it separates in hard, clear, well defined monoclinic prisms, which melt at 126° (corr.). It is easily soluble in water, giving

a solution only faintly alkaline to litmus, sparingly soluble in cold ether or xylene, insoluble in light petroleum, and very readily soluble in the other usual organic solvents. It has very weak basic properties, and can be extracted from a solution in a large volume of benzene by means of concentrated hydrochloric acid, but not by dilute acids:

0.1696 gave 0.4052 CO₂ and 0.1027 H₂O. C = 65.1; H = 6.8.

0.1486 „ 8.7 c.c. N₂ at 19° and 736 mm. N = 6.5.

0.2105 „ 0.4408 AgI. OMe = 27.7.

C₁₂H₁₅O₃N requires C = 65.1; H = 6.9; N = 6.3; OMe = 28.1 per cent.

6:7-Dimethoxy-2-methyltetrahydroisoquinoline (XI, p. 1268).

The crude base is purified by crystallisation of the hydrochloride, regeneration from the pure salt, and crystallisation from light petroleum. It separates from this solvent in clusters of white needles, which contain one-half a molecular proportion of water of crystallisation and melt at 83—84° (corr.). This base is somewhat sparingly soluble in cold water, and very sparingly so in hot water, so that it separates as an oil on warming a cold saturated aqueous solution; it is moderately easily soluble in light petroleum, and very easily so in the other usual organic solvents:

0.1826, air-dried, lost 0.0071 in a vacuum over H₂SO₄. H₂O = 3.9.

C₁₂H₁₇O₂N, $\frac{1}{2}$ H₂O requires H₂O = 4.2 per cent.

0.1582, dried in a vacuum, gave 0.4031 CO₂ and 0.1175 H₂O.

C = 69.5; H = 8.3.

0.1251, dried in a vacuum, gave 7.1 c.c. N₂ at 18° and 766 mm. N = 6.7.

C₁₂H₁₇O₂N requires C = 69.5; H = 8.3; N = 6.8 per cent.

The *hydrochloride* crystallises from moist ethyl acetate in clusters of white, feathery needles, which melt at 216—217° (corr.) and contain nearly one and a-half molecular proportions of water of crystallisation. When this salt is moistened with water, it assumes a pale yellow colour, and crystallises from moist acetone in pale yellow needles, which melt at 59—60° (corr.) and contain three molecules of water of crystallisation; after drying, first in a vacuum desiccator over sulphuric acid and then at 100°, this salt becomes colourless, and melts at 216—217° (corr.). It is easily soluble in water or alcohol, moderately easily so in chloroform, sparingly so in acetone or hot ethyl acetate, and insoluble in ether, benzene, or light petroleum:

0.2109, air-dried salt (from moist ethyl acetate), lost 0.0186 at 100°.

H₂O = 8.8.

0.2681, air-dried salt (from moist acetone), lost 0.0483 at 100°.

H₂O = 18.0.

C₁₂H₁₇O₂N, HCl, $1\frac{1}{2}$ H₂O requires H₂O = 9.9 per cent.

C₁₂H₁₇O₂N, HCl, 3H₂O „ H₂O = 18.2 „

0.1521, dried at 100°, gave 0.3275 CO₂ and 0.1007 H₂O. C = 58.7 ;
H = 7.4.

0.1619, dried at 100°, gave 0.0946 AgCl. Cl = 14.5.

C₁₂H₁₇O₂N, HCl requires C = 59.1 ; H = 7.5 ; Cl = 14.6 per cent.

The *aurichloride* crystallises from absolute alcohol in deep orange, diamond-shaped plates, many of which have the obtuse angles rounded off, and melts at 147° (corr.). It is anhydrous, and is sparingly soluble in water and alcohol :

0.1627 gave 0.0585 Au. Au = 36.0.

C₁₂H₁₈O₂NCl₄Au requires Au = 36.0 per cent.

The *picrate* crystallises from absolute alcohol in broad, yellow needles, which melt at 159—160° (corr.).

Bis(4 : 5-Dimethoxy-2-β-methylaminoethylbenzylidene)-acetone
(XIII, p. 1268).

Two grams of 6 : 7-dimethoxy-2-methyl-3 : 4-dihydroisoquinolinium chloride were dissolved in 20 c.c. of water, and 20 c.c. of 10 per cent. aqueous sodium hydroxide were added. To the clear solution 1 c.c. of acetone was added. The solution remained bright for about a minute, and then suddenly began to deposit oil. After several hours, the deposit, which had become crystalline, was collected, washed with cold water, and dried. The yield amounted to 0.65 gram, that is, 37 per cent. of the theoretical.

Bis(4 : 5-Dimethoxy-2-β-methylaminoethylbenzylidene)-acetone crystallises from moist ether in long, white, glistening needles, which contain four molecules of water of crystallisation, and melt at 77° (corr.) after softening at 75°; after dehydration in a vacuum desiccator over sulphuric acid, it loses water and becomes amorphous, and on then adding to it absolute ether, the base momentarily dissolves, and immediately separates again in colourless, prismatic needles, which are anhydrous and melt at 107—108° (corr.).

Both the hydrated and anhydrous varieties are stable in moist air. The base is very sparingly soluble in water or light petroleum, and sparingly so in ether, but easily soluble in the other usual organic solvents. It decomposes on prolonged heating at 100° :

0.1535 hydrated base gave 0.3392 CO₂ and 0.1119 H₂O. C = 60.3 ;
H = 8.2.

0.1609 hydrated base gave 7.1 c.c. N₂ at 16° and 762 mm. N = 5.2.

0.2650 ,, ,, lost 0.0356 in a vacuum over H₂SO₄.
H₂O = 13.4.

C₂₇H₃₅O₅N₂.4H₂O requires C = 60.0 ; H = 8.2 ; N = 5.2 ; H₂O = 13.3
per cent.

0·1593 anhydrous base gave 0·4043 CO₂ and 0·1093 H₂O. C = 69·2 ;
H = 7·7.

0·1524 anhydrous base gave 7·6 c.c. N₂ at 15° and 768 mm. N = 5·9.
C₂₇H₃₆O₅N₂ requires C = 69·2 ; H = 7·8 ; N = 6·0 per cent.

Molecular-weight determination by the cryoscopic method :

0·1225 in 18·81 benzene gave $\Delta t = 0\cdot072$. M.W. = 443.

0·2822 ,, 18·81 ,, ,, $\Delta t = 0\cdot171$. M.W. = 430.

C₂₇H₃₆O₅N₂ requires M.W. = 468.

The *dihydrochloride* crystallises from water in colourless prisms, which contain three molecules of water of crystallisation, and decompose at about 188° (corr.). It is sparingly soluble in cold water, giving a neutral solution, and very sparingly so in alcohol :

0·1712, air-dried, gave 0·3419 CO₂ and 0·1139 H₂O. C = 54·5 ; H = 7·5.

0·1143 ,, ,, 4·3 c.c. N₂ at 16° and 767 mm. N = 4·4.

0·5626 ,, lost 0·0497 at 100°. H₂O = 8·8.

C₂₇H₃₆O₅N₂·2HCl·3H₂O requires C = 54·4 ; H = 7·5 ; N = 4·7 ;
H₂O = 9·1 per cent.

0·1509, dried at 100°, gave 0·3315 CO₂ and 0·0941 H₂O. C = 59·9 ;
H = 7·0.

0·1361, dried at 100°, gave 0·0725 AgCl. Cl = 13·2.

C₂₇H₃₆O₅N₂·2HCl requires C = 59·9 ; H = 7·1 ; Cl = 13·1 per cent.

This salt dissolves in cold water, giving a colourless solution, which becomes turbid on the addition of aqueous sodium carbonate, owing to the separation of the corresponding base. If, however, the aqueous solution of the hydrochloride is warmed, it quickly becomes yellow, and, after heating for some time, the addition of aqueous sodium carbonate no longer causes turbidity ; on then evaporating the solution, the residue is found to be pure 6 : 7-dimethoxy-2-methyl-3 : 4-dihydroisoquinolinium chloride.

WELLCOME CHEMICAL WORKS,
DARTFORD, KENT.

CXLIII.—*The Morphotropic Relationships between the Derivatives of Picric Acid.*

By GEORGE JERUSALEM.

THE work done during recent years by Barlow and Pope (Trans., 1906, 89, 1675 ; 1907, 91, 1150 ; 1908, 93, 1528) furnishes a method for investigating crystal structure which has led to the solution, in general

terms, of the problem involved in the relation between crystalline form and chemical composition and constitution, and to its practically complete solution in a large number of specific cases. The application of the new method of treatment leads to the conclusion that, in any particular crystalline substance, each atom appropriates to its own occupation an amount of space approximately proportional to the lowest or fundamental valency of the element concerned. The clue thus provided to the volume signification of valency led Le Bas (*Trans.*, 1907, **91**, 112; *Phil. Mag.*, 1907, [vi], **14**, 324; 1908, [vi], **16**, 60) to a rigid proof that in liquid organic substances the same relation holds between atomic volume and valency.

Le Bas showed that the atomic volumes of carbon and hydrogen are in the ratio of four to one in the higher normal paraffins, and that on comparing a number of members of the series under corresponding temperature conditions, the atomic volume of either element remains constant throughout the series. No method has been yet devised for directly determining what are corresponding temperatures for a series of solid crystalline substances, but Barlow and Pope's results indicate that such temperatures would be those at which the molecular volumes, V , are directly proportional to the sum of the valencies of the atoms composing the molecule, the so-called valency volume, W .

In their comparison of the crystalline forms of related substances, these authors therefore calculated the so-called equivalence parameters, $x:y:z$, as the dimensions of a parallelepipedon having the volume, W , and the relative lengths of sides given by the crystallographic axial ratios. A series of sets of equivalence parameters may thus be calculated for a series of related substances which indicates, under corresponding conditions, the morphotropic effect of the chemical substitutions which convert the various substances one into the other.

The melting points—which are approximately corresponding temperatures—of the normal paraffins containing from 11 to 35 atoms of carbon in the molecule only change progressively from -26.5° to $+74.7^{\circ}$; there appears hence but little reason to anticipate that, in a series of very closely related substances containing the same elements in not widely differing proportions, corresponding temperatures would differ very greatly.

If the Barlow-Pope conclusion concerning the relation between valency and volume be correct, it would thus be expected that an approximate proportionality would exist between the molecular volumes, determined at the same temperature, and the valency volumes of a series of such closely related compounds as the picrates and styphnates of organic bases. A new and independent method of testing the accuracy of the conclusion as to the proportionality of valency and volume is thus rendered available, and is applied in the

present paper. The molecular volumes of a number of picrates and styphnates of organic bases have been determined, and it is shown that the ratio, $V/W = R$, of the molecular and the valency volumes does not vary by more than + or - 4 per cent. A confirmation is thus provided of the law of valency volumes.

From a study of the crystalline forms exhibited by aromatic substances, Barlow and Pope derived a very important conclusion concerning the disposition of the component atoms in the crystal structures assumed by benzene and large numbers of its derivatives; this conclusion is to the effect that in the crystal structures of benzene and many of its derivatives the carbon atoms are arranged in columns throughout the crystalline material. The spheres of influence, within which are situated the carbon atoms, are arranged in sets of three in triangular contact, and such sets of three are packed one upon the other so as to form the continuous columns described (Trans., 1906, 89, 1693). In crystalline benzene these columns of carbon spheres are packed together in such a manner that just sufficient space is left for the accommodation of the requisite proportion of hydrogen spheres of atomic influence to make up the molecular composition of benzene; in the crystalline derivatives of benzene the columns of carbon spheres are pushed apart to an extent sufficient to allow of the introduction of the substituting groups, but the continuity of the carbon columns is not broken.

As previously indicated (*Proc. Roy. Soc.*, 1908, 80, A, 557), a direct method can be devised of testing the validity of the conclusions as to the existence of these columns of carbon spheres. That equivalence parameter which measures the height of two links or layers in the carbon column measures the height of the benzene molecule on a scale obtained by taking the volume of a univalent sphere of atomic influence as unity; if the carbon columns remain unbroken in the derivatives of benzene, the particular equivalence parameter referred to must recur amongst the equivalence parameters of all such derivatives. Of the equivalence parameters of benzene, $x:y:z = 3.101 : 3.480 : 2.780$, the third, $z = 2.780$, represents the lengths of two links in the carbon column. It has been already shown that a value approximating closely to this occurs among the equivalence parameters of a number of derivatives of picric acid, and since these substances lend themselves readily to crystallographic measurement, I have prepared and measured a large number of them, the results being recorded in the present paper.

The close-packed assemblage representing benzene itself, to which reference has just been made, is termed the hexagonal benzene assemblage (*H*) in allusion to its mode of derivation. Another, which Barlow and Pope traced amongst certain benzene derivatives, is termed,

for similar reasons, the rhombohedral benzene assemblage (R); it differs dimensionally from the hexagonal one in that its z value is rather smaller than that of the latter, and also because in certain cases it may lead to pseudo-cubic crystal structures (C) in which the identity of the z value becomes lost. It will be shown that all the aromatic substances dealt with in the present paper possess equivalence parameters identifying them with one or other of these three types

In the following descriptions the crystalline system and axial ratios are stated, together with the valency volume, W , and the equivalence parameters and molecular distance ratios, $\chi : \psi : \omega$. The latter values are calculated from the densities, d , determined on the crystalline materials. For the purpose of demonstrating the fact that the molecular volumes, V , are nearly proportional to the valency volume, W , the quantity, $R = V/W$, which should be constant if the proportionality were exact, is also stated. The densities were determined by measuring the density of mixtures of a light and a heavy liquid of the same density as the crystals immersed in them; as for the present purpose it is only necessary to determine the densities with an accuracy of about one part in a thousand, it is superfluous to state the details of the determination in each case.

Ammonium Picrate.

Crystal system: Orthorhombic (*Proc. Roy. Soc.*, 1908, 80, A, 557):

$$\begin{aligned} a : b : c &= 1.8914 : 1 && : 1.3871. \\ x : y : z &= 5.251 : 2.776 : 3.582. && W=56. \quad R=2.557. \\ \chi : \psi : \omega &= 7.174 : 3.794 : 5.262. && d=1.719. \quad V=143.2. \end{aligned}$$

The substance is of the hexagonal type (H), and its y value approximates to the value, $z = 2.780$, of benzene.

Picric Acid.

Crystal system: Orthorhombic (Brugnatelli, *Zeitsch. Kryst. Min.*, 1905, 40, 360):

$$\begin{aligned} a : b : c &= 1.0305 : 1 && : 1.0434. \quad W=50. \quad R=2.594. \\ x : y : z &= 3.706 : 3.596 : 3.752. \\ \chi : \psi : \omega &= 5.094 : 4.941 : 5.153. && d=1.767. \quad V=129.7. \end{aligned}$$

Styphnic Acid (*Proc. Roy. Soc.*, 1908, 80, A, 562).

Crystal system: Hexagonal; $a : c = 1 : 1.3890$.

On referring this axial ratio to orthorhombic axes, the following values result:

$$\begin{aligned} a : b : c &= 1.7321 : 1 && : 1.3890. \\ x : y : z &= 4.825 : 2.786 : 3.869. && W=52. \quad R=2.577. \\ \chi : \psi : \omega &= 6.615 : 3.819 : 5.305. && d=1.829. \quad V=134.1. \end{aligned}$$

The substance is of the hexagonal type (*H*), and its γ value approximates to the value, $z = 2.780$, of benzene.

Monomethylamine Picrate.

This salt was prepared by Delépine (*Ann. Chim. Phys.*, 1896, [vii], 8, 461) and Ristenpart (*Ber.*, 1896, 29, 2530). It crystallises from ethyl acetate in large, straw-yellow crystals melting at 215°.

Crystal system: Orthorhombic; $a : b : c = 2.3361 : 1 : 1.1529$.

Forms observed: $a\{100\}$, $c\{001\}$, $r\{101\}$, $o\{111\}$.

The following angular measurements were obtained:

Angle.	Number of observations.	Limits.	Mean.	Calculated.
100 : 101	26	63°34'— 64° 9'	63°44' 0"	—
100 : 111	24	71 53 — 72 17	72 4 50	—
101 : 111	20	45 44 — 46 19	45 56 40	45°57'10"
001 : 111	20	51 15 — 51 37	51 26 30	51 25 50
101 : 001	14	25 41 — 26 37	26 18 40	26 16 0
111 : 111	9	35 45 — 35 54	35 50 0	35 50 20

Before calculating the following values, the axial dimension a was divided by two:

$$x : y : z = 4.186 : 3.584 : 4.132. \quad W = 62. \quad R = 2.488.$$

$$\chi : \psi : \omega = 5.672 : 4.857 : 5.599. \quad d = 1.687. \quad V = 154.2.$$

The close approximation of the γ value for monomethylamine picrate to that of picric acid indicates that this substance is of the pseudo-cubic type (*C*); its equivalence parameters and molecular distance ratios are very closely related to those of picric acid. The form $a\{100\}$ is much the largest, and the other forms are well developed.

Dimethylamine Picrate.

This substance was also prepared by Delépine (*loc. cit.*, 459), and separates from alcohol or dilute acetone in straw-yellow crystals melting at 158—159°.

Crystal system: Orthorhombic; $a : b : c = 1.9222 : 1 : 0.90049$.

Forms: $a\{100\}$, $r\{101\}$, $o\{111\}$, $w\{211\}$, $b\{010\}$.

The following measurements were obtained:

Angle.	Number of observations.	Limits.	Mean.	Calculated.
100 : 111	32	70°36'— 70°57'	70°48'20"	—
010 : 111	20	50 38 — 50 53	50 48 20	—
100 : 101	15	64 48 — 64 56	64 53 10	64°53'50"
100 : 211	11	55 2 — 55 18	55 9 30	55 9 10
010 : 211	12	56 27 — 56 56	56 41 40	56 41 20
111 : 111	10	38 19 — 38 29	38 21 20	38 23 20
111 : 101	12	39 7 — 39 16	39 11 40	39 11 40

The form $a\{100\}$ is always dominant; $w\{211\}$ is very rarely seen on crystals from alcohol, but is always present on those from dilute

acetone. No distinct cleavage is observed. After multiplying the unit length along the axis c by two, the following values of equivalence parameters and molecular distance ratios are obtained:

$$\begin{aligned}x : y : z &= 5.186 : 2.698 : 4.859. & H^- &= 68. \\ \chi : \psi : \omega &= 7.152 : 3.721 : 6.702. & V &= 178.4. \\ d &= 1.538. & R &= 2.622.\end{aligned}$$

The substance therefore belongs to the hexagonal type of marshaling (*II*), and both sets of parameters approximate very closely to the corresponding values quoted for ammonium picrate. The y values of the dimethylamine and the ammonium and potassium salts are almost identical, namely:

Potassium Salt: $x : y : z = 5.082 : 2.698 : 3.647$ (*Proc. Roy. Soc.*, 1908, 80, A, 560).

A distinct morphotropic relationship is apparent between mono- and di-methylamine picrate; this is expressed in the following statement of fundamental angles:

Angle.	Monomethyl- amine pi-rate.	Dimethyl- amine pi-rate.
100 : 101	63° 44' 0"	64° 53' 50"
100 : 111	72 4 50	70 48 20
101 : 111	45 57 10	49 11 40

Ethylamine Picrate.

This salt was prepared by Smolka (*Monatsh.*, 1885, 6, 917) and melts at 170°. Large, straw-yellow crystals are deposited from ethyl acetate solutions.

Crystal system: Monosymmetric; $a : b : c = 2.2768 : 1 : 1.5350$;
 $\beta = 92^\circ 27' 20''$.

Forms: $a\{100\}$, $c\{001\}$, $o\{111\}$, $r\{101\}$, $r'\{10\bar{1}\}$, $w\{11\bar{1}\}$, $p\{210\}$.

The following angular measurements were obtained:

Angle.	Number of observations.	Limits.	Mean.	Calculated.
100 : 001	16	87° 10' — 87° 46'	87° 32' 40"	—
001 : 101	18	34 26 — 34 53	34 44 40	—
101 : 111	17	52 7 — 52 36	52 22 50	—
001 : 111	19	59 41 — 60 17	59 55 20	59° 53' 50"
101 : 111	9	51 12 — 51 26	51 18 20	51 16 30
100 : 111	13	70 40 — 71 16	70 59 20	70 58 10
001 : 101	4	32 57 — 33 17	33 10 0	33 12 40
100 : 101	3	54 19 — 54 21	54 19 40	54 20 0
001 : 111	8	58 18 — 58 34	58 25 20	58 26 20
100 : 001	13	92 12 — 92 43	92 26 50	92 27 20
101 : 100	10	57 27 — 57 56	57 40 20	57 40 40
111 : 111	6	40 14 — 40 30	40 23 50	40 25 20
100 : 210	2	48 7 — 48 20	48 16	48 40 40

No distinct cleavage plane is observed, and $p\{210\}$ is rare and always very small. The following values were obtained:

$$\begin{aligned}x : y : z &= 6.126 : 2.691 : 4.130. & \beta &= 92^\circ 27' 20''. \\ \chi : \psi : \omega &= 8.324 : 3.656 : 5.611. \\ H^- &= 68. & V &= 170.6. & d &= 1.608. & R &= 2.509.\end{aligned}$$

The y value is practically identical with that of the isomeric dimethylamine picrate, for which

$$x : y : z = 5.186 : 2.698 : 4.859,$$

and in the passage from ammonium picrate, with

$$x : y : z = 5.251 : 2.776 : 3.852,$$

to dimethylamine picrate the main increase falls upon the parameter x ; in passing to ethylamine picrate, the x parameter of the ammonium salt suffers the largest increase.

As the factor R is nearly constant throughout the series of salts now considered, the same relationships are exhibited in this and in the following cases by the molecular distance ratios as by the equivalence parameters.

Triethylamine Picrate, $\text{Et}_3\text{N}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{OH}$.

This salt has not been previously described, and was prepared by mixing hot aqueous solutions of triethylamine hydrochloride and calcium picrate and allowing to cool. *Triethylamine picrate*, being sparingly soluble in cold water, separates, and is purified by crystallisation from hot alcohol; it melts at 173° , and is very soluble in ethyl acetate or acetone, giving solutions from which bright straw-yellow crystals are deposited:

0.1355 gave 20.2 c.c. N_2 (moist) at 17° and 764 mm. $\text{N} = 17.31$.

$\text{C}_{12}\text{H}_{18}\text{O}_7\text{N}_4$ requires $\text{N} = 17.00$ per cent.

Crystal system: Orthorhombic; $a : b : c = 2.9752 : 1 : 1.5751$.

Forms observed: $a\{100\}$, $r\{101\}$, $c\{001\}$, $p\{210\}$, $q\{011\}$, $q'\{021\}$, $b\{010\}$.

The following angular measurements were obtained:

Angle.	Number of observations.	Limits.	Mean.	Calculated.
100 : 101	24	$61^\circ 57\frac{1}{2}' - 62^\circ 20'$	$62^\circ 6' 10''$	—
001 : 011	25	$57\ 25 - 57\ 42$	$57\ 35\ 20$	—
210 : 100	17	$55\ 55 - 56\ 19$	$56\ 4\ 50$	$56^\circ 5' 20''$
021 : 001	7	$72\ 14 - 72\ 35$	$72\ 27\ 20$	$72\ 23\ 20$
011 : 101	8	$61\ 38 - 61\ 45$	$61\ 42\ 30$	$61\ 43\ 30$
011 : 210	11	$45\ 27 - 45\ 34$	$45\ 30\ 50$	$45\ 31\ 10$
101 : 001	14	$27\ 29 - 28\ 2$	$27\ 51\ 40$	$27\ 53\ 50$

The form $a\{100\}$ is dominant, $q'\{021\}$ is very small, and $b\{010\}$ was only observed in one instance; there is a poor cleavage on $c\{001\}$:

$$x : y : z = 8.026 : 2.698 : 4.249.$$

$$\chi : \psi : \omega = 11.030 : 3.708 : 5.840.$$

$$W = 92. \quad V = 238.8. \quad d = 1.383. \quad R = 2.596.$$

The introduction of a second and third ethyl group into monoethylamine picrate has thus been accompanied by a large increase in the parameter x , that of y has remained practically unchanged, and that of z has increased very slightly.

Tetraethylammonium Picrate, $C_6H_2(NO_2)_3 \cdot ONEt_4$.

This salt was first prepared by Lossen (*Annalen*, 1876, 181, 375), who gives the melting point as 249—251°; the material now examined melted at 254°. Very good, although small, orange-coloured crystals are obtained from ethyl acetate solutions.

Crystal system: Monosymmetric; $a : b : c = 2.9909 : 1 : 1.6075$; $\beta = 92^\circ 55' 20''$.

Forms observed: $a\{100\}$, $r\{101\}$, $r'\{10\bar{1}\}$, $m\{210\}$, $o\{111\}$, $w\{11\bar{1}\}$.

The following angular measurements were obtained:

Angle.	Number of observations.	Limits.	Mean.	Calculated.
100 : 101	27	59°12' — 59°37'	59°29'40"	—
100 : 10 $\bar{1}$	25	63 52 — 64 10	64 1 40	—
210 : 100	24	55 53 — 56 22	56 11 40	—
111 : 101	19	53 57½ — 54 22	54 9 30	54°10'10"
11 $\bar{1}$: 10 $\bar{1}$	9	55 0 — 55 23½	55 11 40	55 19 10
101 : 111	9	70 55 — 71 13	71 3 40	71 8 20
10 $\bar{1}$: 210	10	75 43 — 76 2	75 53 0	75 53 40
101 : 210	7	73 24 — 73 44	73 32 50	73 35 40
101 : 11 $\bar{1}$	6	71 21 — 71 52	71 41 50	71 41 10
11 $\bar{1}$: 210	7	34 38 — 35 2	34 45 50	34 43 10
101 : 10 $\bar{1}$	26	56 14 — 56 42	56 28 10	56 28 40

The form $c\{001\}$ is dominant, whilst $o\{111\}$ and $w\{11\bar{1}\}$ are, in general, small. It is noteworthy that, with the exception of the pinacoid $c\{001\}$, the same forms are observed as on monoethylamine picrate:

$$x : y : z = 8.337 : 2.788 : 4.481. \quad \beta = 92^\circ 55' 20''.$$

$$x : \psi : \omega = 11.277 : 3.769 : 6.063.$$

$$W = 104. \quad V = 257.3. \quad R = 2.474. \quad d = 1.393.$$

The parameter y is slightly larger than in the case of mono- and tri-ethylamine picrates, but the main increase in the valency volume is still borne by the parameter x ; the morphotropic relationship thus involved is shown in the close similarity of the observed angles in the zones [010] and [001] on the two substances:

Angle.	Triethyl- amine salt.	Tetraethyl- ammonium salt.
100 : 101	62° 6' 10"	59° 29' 40"
101 : 10 $\bar{1}$	55 47 40	56 28 40
100 : 210	56 5 20	56 11 40

Aniline Picrate.

Large measurable crystals of this substance are obtained from alcohol; they are of a dark green colour, and give measurements identical with those made on red crystals which are deposited from aqueous solutions.

Crystal system: Monosymmetric; $a : b : c = 3.7120 : 1 : 2.1048$; $\beta = 92^\circ 47' 50''$.

Forms observed : $a\{100\}$, $c\{001\}$, $n\{011\}$, $r\{101\}$, $r'\{10\bar{1}\}$, $p\{20\bar{1}\}$.

The following angular measurements were obtained :

Angle.	Number of observations.	Limits.	Mean.	Calculated.
100 : 001	17	86°50' — 87°36'	87°12'10"	—
001 : $\bar{1}01$	14	29 58 — 30 23	30 13 10	—
001 : 011	22	61 6 — 64 53	64 33 40	—
001 : 101	7	28 43½ — 29 19	28 54 0	28°51'30"
100 : 101	6	57 56 — 58 33	58 19 0	58 20 30
$\bar{1}01$: 011	5	68 1 — 68 28	68 11 10	68 12 40
100 : 011	10	88 30 — 89 0	88 44 10	88 47 55
10 $\bar{1}$: 20 $\bar{1}$	3	19 16 — 19 34	19 24 0	19 57 10
100 : 00 $\bar{1}$	15	92 22½ — 92 57	92 47 0	92 47 50
011 : 01 $\bar{1}$	7	50 40 — 51 20	50 52 50	50 52 40

The forms $a\{100\}$, $c\{001\}$, $n\{011\}$ are equally well developed ; $p\{20\bar{1}\}$ is only present on the red crystals from water. There is a perfect cleavage parallel to $a\{100\}$. After dividing unit length along the axis c by two, the following values are obtained :

$$x : y : z = 5.163 : 2.782 : 5.855. \quad \beta = 92^\circ 47' 50".$$

$$x : \psi : \omega = 6.973 : 3.757 : 7.909.$$

$$W = 84. \quad V = 207.0. \quad d = 1.558. \quad R = 2.464.$$

On comparing the equivalence parameters first stated with the values for ammonium picrate,

$$x : y : z = 5.251 : 2.776 : 3.852,$$

it is seen that the value x is only slightly different, and that the value y has remained the same within the errors of measurement, and is the same as the z value for the hexagonal benzene assemblage (H). The result of the introduction of a phenyl group into ammonium picrate is therefore morphotropically very simple.

Besides the above-quoted picrates, a large number of others were crystallised from different solvents, but could not be obtained in measurable crystals, or were anorthic and thus of no immediate value for our present purpose. When it was possible to obtain large crystals, the densities were determined in order to test the constancy of the quantity R . The following salts were thus examined.

Benzylamine Picrate, $\text{CH}_2\text{Ph}\cdot\text{NH}_2, \text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{OH}$,

has been described by Moureu and Lazennec (*Compt. rend.*, 1906, 143, 553). It was prepared by adding benzylamine to a solution of an equivalent amount of picric acid in boiling water. After crystallisation from hot alcohol, it melts at 195—199° :

0.1740 gave 24.9 c.c. N_2 (moist) at 16.5° and 766 mm. $\text{N} = 16.69$.

$\text{C}_{13}\text{H}_{12}\text{O}_7\text{N}_4$ requires $\text{N} = 16.66$ per cent.

Anorthic crystals are deposited from ethyl acetate solutions.

$$W = 90. \quad V = 218.9. \quad d = 1.536. \quad R = 2.433.$$



was described by Carrasco and Padoa (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 699). It was prepared in a similar way to the foregoing compound, and is also nearly insoluble in water. After crystallisation from alcohol, it melts and decomposes at 212—215°:

0.2481 gave 36.1 c.c. N_2 (moist) at 18° and 762 mm. $N = 16.85$.

$C_{13}H_{12}O_7N_4$ requires $N = 16.66$ per cent.

Badly developed, monoclinic crystals are deposited from alcoholic solutions:

$$W = 90. \quad V = 218.5. \quad d = 1.539. \quad R = 2.428.$$

m-Toluidine Picrate.

This salt was prepared and purified in a similar way to the above mentioned. It decomposed when heated above 180°:

0.1400 gave 20.1 c.c. N_2 (moist) at 17° and 764 mm. $N = 16.75$.

$C_{13}H_{12}O_7N_4$ requires $N = 16.66$ per cent.

Striated, monoclinic crystals are obtained by crystallisation from cold alcohol:

$$W = 90. \quad V = 225.6. \quad d = 1.491. \quad R = 2.506.$$

For the sake of comparison, the equivalence parameter of naphthalene picrate (*Atti Soc. Ital. sci. nat.*, 1902, 41, 15) and of the additive compound of naphthalene and trinitrobenzene (*R. Accad. sci. Bologna*, Sessione del 10 Novembre 1907), both of which were measured by Boëris, may be stated here. The axial ratios of these substances are:

$$\begin{aligned} C_{10}H_8, C_6H_2(NO_2)_3 \cdot OH. \\ a : b : c = 2.5582 : 1 : 4.1846. \\ \beta = 83^\circ 12'. \end{aligned}$$

$$\begin{aligned} C_{10}H_8, C_6H_2(NO_2)_3. \\ a : b : c = 2.3170 : 1 : 4.0961. \\ \beta = 83^\circ 24'. \end{aligned}$$

After dividing unit length along the axis c by two, the following equivalence parameters are obtained:

$$\begin{aligned} C_{10}H_8, C_6H_2(NO_2)_3 \cdot OH. \\ W = 98. \\ x : y : z = 6.401 : 2.715 : 5.680. \\ \beta = 96^\circ 48'. \end{aligned}$$

$$\begin{aligned} C_{10}H_8, C_6H_2(NO_2)_3. \\ W = 96. \\ x : y : z = 6.327 : 2.731 : 5.593. \\ \beta = 96^\circ 36'. \end{aligned}$$

The following values for naphthalene picrate were found by determining its density:

$$\begin{aligned} V = 233.5. \quad d = 1.530. \quad R = 2.382. \\ \chi : \psi : \omega = 8.549 : 3.625 : 7.586. \\ \beta = 96^\circ 48'. \end{aligned}$$

The value y is again very near the z value for the hexagonal benzene assemblage (H), and both x and z have increased considerably in comparison with the corresponding dimensions for ammonium picrate.

Monomethylamine Styphnate, $\text{NH}_2\text{Me}, \text{C}_6\text{H}(\text{OH})_2(\text{NO}_2)_3$.

This salt is obtained by mixing equivalent amounts of monocalcium styphnate and methylamine hydrochloride in hot aqueous solution and evaporating; it separates as a bright yellow, crystalline powder, and is purified by crystallisation from alcohol. The salt melts at 191° , is very soluble in acetone, and moderately so in water or alcohol; good crystals for goniometric measurements are obtained with difficulty, but fairly satisfactory ones were deposited from solutions in ethyl acetate, the salt being rather less soluble in this than in the other solvents mentioned.

The base distilled from 0.3100 gram, after addition of lime and water, neutralised 11.45 c.c. of sulphuric acid containing 0.04907 gram per c.c.:

$$\text{MeNH}_2 = 11.49.$$

$$\text{C}_7\text{H}_8\text{O}_8\text{N}_4 \text{ requires } \text{MeNH}_2 = 11.26 \text{ per cent.}$$

Crystal system: Monosymmetric; $a:b:c = 0.5232:1:0.3716$; $\beta = 103^\circ 4' 10''$.

Forms observed: $b\{010\}$, $c\{001\}$, $p\{110\}$, $q\{011\}$.

The following angular measurements were obtained:

Angle.	Number of observations.	Limits.	Mean.	Calculated.
010 : 011	13	69°50' — 70°21'	70° 6' 0"	—
010 : 110	14	62 36 — 63 26	62 59 40	—
001 : 110	16	78 5 — 78 43	78 22 40	—
001 : 011	9	19 41 — 20 8	19 56 30	19°54' 0"
110 : 110	14	101 17 — 101 55	101 33 40	101 37 20

The form $q\{011\}$ was but rarely observed, and was always very small; there is a perfect cleavage parallel to $p\{110\}$, and the faces of all the forms give multiple reflections on the goniometer. After dividing unit length along the axis b by four, the following values are obtained:

$$x:y:z = 5.785 : 2.764 : 4.109. \quad \beta = 103^\circ 4' 10''.$$

$$x:\psi:\omega = 7.904 : 3.777 : 5.614.$$

$$W=64. \quad V=163.2. \quad d=1.692. \quad R=2.551.$$

The equivalence parameter γ has nearly the same value as in the case of ammonium picrate, namely, 2.776; close correspondence between the molecular distance parameters, ψ , is also to be noted, the values being respectively 3.777 and 3.794.

Dimethylamine Styphnate, $\text{NHMe}_2, \text{C}_6\text{H}(\text{OH})_2(\text{NO}_2)_3$.

The preparation of this salt is similar to that of the previous one, and yields a bright yellow, crystalline substance, which melts at 208°

after crystallisation from alcohol. The salt is sparingly soluble in water, dissolves more readily in alcohol, and still more easily in acetone and ethyl acetate:

0.2072 gave 34.3 c.c. N_2 (moist) at 16° and 770 mm. $N = 19.57$.

$C_8H_{10}O_8N_4$ requires $N = 19.31$ per cent.

Measurable crystals were obtained from acetone solutions.

Crystal system: Monosymmetric; $a:b:c = 1.5897:1:1.2606$; $\beta = 68^\circ 5' 10''$.

Forms observed: $a\{100\}$, $m\{110\}$, $q\{011\}$, $c\{001\}$.

The following angular measurements were obtained:

Angle.	Number of observations.	Limits.	Mean.	Calculated.
110 : 100	27	$55^\circ 31' - 56^\circ 7'$	$55^\circ 51' 40''$	—
100 : 011	19	$75^\circ 43' - 76^\circ 19'$	$75^\circ 57' 50''$	—
011 : $\bar{0}\bar{1}\bar{1}$	15	$98^\circ 38' - 99^\circ 14'$	$98^\circ 55' 50''$	—
100 : 001	2	$68^\circ 16' - 68^\circ 23'$	$68^\circ 19' 0''$	$68^\circ 5' 10''$
110 : 011	13	$39^\circ 44' - 40^\circ 10'$	$39^\circ 53' 30''$	$40^\circ 5' 0''$
$\bar{1}\bar{1}0$: 011	9	$60^\circ 24' - 60^\circ 37'$	$60^\circ 30' 0''$	$60^\circ 28' 10''$
011 : 001	8	$49^\circ 14' - 49^\circ 44'$	$49^\circ 30' 40''$	$49^\circ 28' 0''$
110 : $\bar{1}\bar{1}0$	13	$68^\circ 0' - 68^\circ 39'$	$68^\circ 14' 10''$	$68^\circ 16' 40''$

The axial ratios of this salt show clearly that this is pseudo-hexagonal, and it is therefore convenient to change the indices of the forms present so that the axial directions become pseudo-rectangular. This may be done by changing the indices 100, 001, 110, 011 respectively to 100, $10\bar{1}$, 210, $01\bar{1}$. The axial ratios then become

$$a : b : c = 2.9503 : 1 : 1.2606.$$

$$\beta = 91^\circ 26' 20''.$$

Whence the following values are calculated:

$$x : y : z = 7.849 : 2.660 : 3.354.$$

$$\chi : \psi : \omega = 10.836 : 3.673 : 4.632. \quad \beta = 91^\circ 26' 20''.$$

$$W = 70. \quad V = 184.3. \quad d = 1.575. \quad k = 2.633.$$

Trimethylamine Styphnate, $NMe_3 \cdot C_6H(OH)_2(NO_2)_3$.

This salt was obtained in the same way as the preceding one, and is sparingly soluble in alcohol, more so in acetone, and almost insoluble in ethyl acetate. After purification by crystallisation from acetone solution, it forms a bright yellow, crystalline powder, which decomposes gradually on heating to above 200° :

0.1492 gave 23.9 c.c. N_2 (moist) at 14° and 752 mm. $N = 18.72$.

$C_9H_{12}O_8N_4$ requires $N = 18.42$ per cent.

Small but, in some zones, very brilliant crystals are obtained from acetone solution.

Crystal system: Orthorhombic; $a:b:c = 2.9160:1:1.3494$.

Forms observed: $a\{100\}$, $r\{101\}$, $p\{210\}$, $q\{011\}$.

The following angular measurements were obtained :

Angle.	Number of observations.	Limits.	Mean.	Calculated.
210 : 210	16	68°46' — 69° 0'	68°53'30"	—
210 : 011	18	48 21 — 48 40	48 30 20	—
011 : 011	8	73 4 — 73 22	73 9 20	73° 5' 0"
101 : 100	5	65 1 — 65 8	65 4 20	65 10 0
101 : 210	16	76 0 — 76 20	76 10 20	76 15 30
100 : 210	12	55 20 — 55 39	55 31 20	55 33 20

The forms lying in the zone [010] are the largest, but do not give good reflections on the goniometer. There is a good cleavage parallel to $b\{010\}$. The following values were obtained :

$$x : y : z = 7.824 : 2.683 : 3.621.$$

$$\chi : \psi : \omega = 10.840 : 3.717 : 5.015.$$

$$W = 76. \quad V = 202.1. \quad d = 1.506. \quad R = 2.659.$$

It will be seen that both the equivalence parameters and the molecular distance ratios correspond closely with those of dimethylamine styphnate.

Monoethylamine Styphnate, $\text{NH}_2\text{Et}, \text{C}_6\text{H}(\text{OH})_2(\text{NO}_2)_3$.

This salt was prepared in the same way as the preceding substances, and, after crystallisation from hot alcohol, forms a yellow powder melting at 138° :

0.1890 gave 30.6 c.c. N_2 (moist) at 16° and 773 mm. $\text{N} = 19.17$.

$\text{C}_8\text{H}_{10}\text{O}_8\text{N}_4$ requires $\text{N} = 19.31$ per cent.

Poorly-developed, anorthic crystals are deposited from solutions in water and alcohol. The density of the substance was determined and the following values found :

$$W = 70. \quad V = 180.0. \quad d = 1.612. \quad R = 2.573.$$

Triethylamine Styphnate, $\text{NEt}_3, \text{C}_6\text{H}(\text{OH})_2(\text{NO}_2)_3$.

This salt was prepared and purified in a similar manner to the preceding ones, and was found to melt at 170° :

0.1782 gave 26.0 c.c. N_2 (moist) at 18° and 748 mm. $\text{N} = 16.58$.

$\text{C}_{12}\text{H}_{18}\text{O}_8\text{N}_4$ requires $\text{N} = 16.18$ per cent.

Large, but not measurable, crystals are obtained from acetone solutions :

$$W = 94. \quad V = 238.3. \quad d = 1.452. \quad R = 2.535.$$

Tetraethylammonium Styphnate, $\text{C}_6\text{H}(\text{OH})(\text{NO}_2)_3\text{O} \cdot \text{NEt}_4$.

This substance was recrystallised from acetone, and explodes on heating at about 210°. It was obtained only in the form of yellow needles, and therefore no density determination was made :

0.1823 gave 23.0 c.c. N_2 (moist) at 13° and 776 mm. $N = 15.21$.

$C_{14}H_{22}O_8N_4$ requires $N = 15.00$ per cent.

It is convenient to summarise the results of the measurements given in the present paper in the following tables; the numerical data relating to the axial ratios, molecular distance ratios, equivalence parameters, molecular volumes, etc., are thus stated.

Table of Axial Ratios and Equivalence Parameters.

Substance.	a	b	c .	Multiples selected. W .	x	y	z .	β .
<i>Substances with Hexagonal Marshalling (H).</i>								
Ammonium picrate.....	1.8914	: 1	: 1.3871	—	56	5.251	: 2.776	: 3.852 90°
Dimethylamine picrate.....	1.9222	: 1	: 0.90049	2c	68	5.186	: 2.698	: 4.859 90
Monoethylamine picrate.....	2.2768	: 1	: 1.5350	—	68	6.126	: 2.691	: 4.130 92 27'20"
Triethylamine picrate.....	2.9752	: 1	: 1.5751	—	92	8.026	: 2.698	: 4.249 90
Tetraethylammonium picrate.....	2.9909	: 1	: 1.6075	—	104	8.337	: 2.788	: 4.481 92 55 20
Aniline picrate	3.7120	: 1	: 2.1048	$a/2$	84	5.163	: 2.782	: 5.855 92 47 50
Naphthalene picrate.....	2.3552	: 1	: 4.1846	$c/2$	98	6.401	: 2.715	: 5.679 96 48
$C_6H_2(NO_2)_3$ $C_{10}H_8$ Styphnic acid	2.3170	: 1	: 4.0961	$c/2$	96	6.327	: 2.731	: 5.593 96 36
Styphnic acid	1.7321	: 1	: 1.3890	—	52	4.825	: 2.786	: 3.869 Hexagonal
Monomethylamine styphnate..	0.5232	: 1	: 0.3716	$b/4$	64	5.785	: 2.764	: 4.109 76 55 50
Dimethylamine styphnate..	2.9503	: 1	: 1.2606	—	70	7.849	: 2.660	: 3.354 91 26 20
Trimethylamine styphnate..	2.9160	: 1	: 1.3494	—	76	7.824	: 2.683	: 3.621 90

Substances with Pseudo-cubic Structures (C).

Picric acid ...	1.0305	: 1	: 1.0434	—	50	3.706	: 3.596	: 3.752 90°
Monomethylamine picrate.....	2.3361	: 1	: 1.1529	$a/2$	62	4.186	: 3.584	: 4.132 90

Table of Densities, Topical Parameters, and Quantities R.

Substance.	χ	ψ	ω .	d .	V .	R .	Crystal system.
<i>Substances with Hexagonal Marshalling (H).</i>							
Ammonium picrate...	7.174	: 3.794	: 5.262	1.719	143.2	2.557	Orthorhombic
Dimethylamine picrate	7.152	: 3.721	: 6.702	1.538	178.4	2.622	„
Monoethylamine picrate	8.324	: 3.656	: 5.611	1.608	170.6	2.509	Monosymmetric
Triethylamine picrate	11.030	: 3.708	: 5.840	1.383	238.8	2.596	Orthorhombic
Tetraethylammonium picrate	11.277	: 3.769	: 6.063	1.393	257.3	2.474	Monosymmetric
Aniline picrate.....	6.973	: 3.757	: 7.909	1.558	207.0	2.464	„
Naphthalene picrate.	8.549	: 3.625	: 7.586	1.530	233.5	2.382	„

Table of Densities, Topical Parameters, and Quantities R (continued).

Substance.	χ	ψ	ω	d .	V .	R .	Crystal system.
<i>Substances with Hexagonal Marshalling (H).</i>							
Styphnic acid	6·615	3·819	5·305	1·829	134·1	2·577	Hexagonal
Monomethylamine styphnate	7·904	3·777	5·614	1·692	163·2	2·551	Monosymmetric
Dimethylamine styphnate	10·836	3·673	4·632	1·575	184·3	2·633	„
Trimethylamine styphnate	10·840	3·717	5·015	1·506	202·1	2·659	Orthorhombic

Substances with Pseudo-cubic Structures (C).

Picric acid	5·094	4·941	5·153	1·767	129·7	2·594	Orthorhombic
Monomethylamine picrate	5·672	4·857	5·599	1·687	154·2	2·488	„

	d .	V .	W .	R .
Monoethylamine styphnate	1·612	180·0	70	2·573
Triethylamine „	1·452	238·3	94	2·535
Piperidine picrate *	1·538	204·3	84	2·433
Benzylamine picrate	1·536	218·9	90	2·433
<i>m</i> -Toluidine „	1·491	225·6	90	2·506
<i>o</i> -Toluidine „	1·539	218·5	90	2·428
Pyridine „ †	1·537	200·5	78	2·571

* Rosenheim and Schidrowitz (Trans., 1898, 73, 143).

† Crystals from ethyl acetate washed with alcohol (Ladenburg, *Annalen*, 1888, 247, 5).

Two remarkable relationships are immediately obvious from an inspection of these tables. The first is that, as already remarked, the α value for the benzene assemblage of hexagonal derivation, namely, $\alpha = 2·780$, recurs with very close numerical approximation in the γ value of each picric and styphnic acid derivative the crystalline form of which indicates a similar hexagonal derivation of the crystalline structure. The second is, that this approximately constant γ value in each case occurs in a direction perpendicular to a plane of symmetry of the crystalline structure.

In addition to these two striking regularities in which the equivalence parameter γ is concerned, it is also to be remarked that the other equivalence parameters, α and α , in most cases change in a regular manner during any given substitution of one group or radicle by another; it is frequently observable that such a substitution brings about an alteration in dimension of only one of these two parameters, α and α , whilst leaving the other almost unchanged. The investigation of these changes in α and α would thus be expected to lead to the discovery of further regularities and to the detection of the laws governing their alterations; for the present, however, it is convenient

to consider only the dimension, y , to which such a definite physical meaning has been attached.

The fact that the examination of so large a number of benzene derivatives as are crystallographically described above indicates that their crystal structures can be regarded as of hexagonal derivation, and that their y values approximate so closely to the z value for benzene itself, constitutes very strong confirmatory evidence in favour of the conclusions previously drawn by Barlow and Pope as to the existence of the continuous columns of carbon spheres, referred to in the early part of this paper, as components of the crystal structures of the benzene derivatives.

The anticipation that, in accordance with the Barlow-Pope interpretation of valency as a volume property, the sums of the valencies should be roughly proportional to the molecular volumes in the case of a series of related crystalline substances, is abundantly fulfilled in the approximate constancy of the ratio, $V/W = R$, for the whole of the members of the series now discussed. The values of the ratio R for these substances are stated in the various tables given above; the mean value of R is 2.560, and the individual values of the ratio are distributed about the mean within the limits expressed by

$$R = 2.560 \pm 4 \text{ per cent.}$$

It thus becomes possible to calculate the molecular volume, V , of a member of the present series within about 4 per cent. as

$$V = 2.560 W.$$

Similarly, the density, d , of a member of the series can be calculated within the same limits of accuracy as

$$d = M/2.560 W,$$

M being the molecular weight of the substance.

As qualitative results from the arguments and conclusions just put forward, it follows:

(1) That the density of a member of the series must diminish as the number of alkyl groups contained in the molecule increases.

This is true throughout the series with the single exception of tetraethylammonium picrate, which has a higher density than triethylamine picrate. It would be supposed, and this is in accordance with the conclusions of Le Bas concerning the molecular volumes of liquid substances under equally reduced conditions, that this apparent exception is connected with the extraordinarily high melting point, 254° , of tetraethylammonium picrate.

(2) The density of a styphnic acid derivative should in each case be greater than that of the corresponding picric acid compound. This is true in all the cases now examined.

From the observation that the ratio $R = V/W$ is so approximately constant throughout the series of picric and styphnic acid derivatives, it is evident that the study of the equivalence parameters and of the molecular distance ratios leads, in the present case, to the same conclusions. It is therefore unnecessary to discuss further the relationships between the molecular distance ratios of the substances now described.

In most cases the equivalence parameters are calculated directly from the axial ratios, using the latter in the form in which they were experimentally determined; in some few instances, as indicated in the text and in the table on p. 1228, one of the axial dimensions has been multiplied or divided by two before proceeding to the calculation of the equivalence parameters or the molecular distance ratios.

As this process of multiplication or division introduces an arbitrary element into the subsequent calculation, it might conceivably be argued that the necessity for this process weakens the conclusions as to the constancy of the equivalence parameter γ , etc. Although the infrequency with which the necessity for the multiplication or division arises, the simplicity of the factors used, and the close agreements of the results obtained, show that such an argument is fallacious, a method was nevertheless devised to show mathematically that the approximate constancy of the parameter γ constitutes a law of nature as opposed to the view that this constancy is devoid of physical meaning, and results merely from the arbitrary multiplication and division of the axial ratios. By taking into account all the different ways by which a value near γ might be found by the alteration of the axial ratios used in the foregoing pages, that is, by a multiplication by 2 or $\frac{1}{2}$ of only one of the unit values in the axial directions, it is possible to state the mean difference of all the values thus found, and to compare this mean difference with the actually observed differences between the γ values in the table of equivalence parameters on p. 1228. In this way it is possible, for example, to calculate the probability that a table of axial ratios, chosen at mere random, will show γ values agreeing with one another within the same limits as the γ values of the table. This probability is found to be much smaller than a magnitude of the order $1/4^{13}$. Details of this method will be published elsewhere.

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

CXLI.V.—*The Colour and Constitution of Azo-compounds. Part III.*

By JOHN THEODORE HEWITT and WILLIAM THOMAS.

RATHER more than a year ago one of the authors of the present communication, jointly with J. J. Fox, published an account of some mixed single azo-compounds, the benzene nucleus on the one side of the azo-group being substituted in the para-position by a dimethyl-amino- or trimethylammonium group, whilst the other nucleus, in this case naphthalene, contained hydroxyl in the α -position, the azo-group having entered the naphthalene in position 4 (Trans., 1908, 93, 333). The results showed that if to substances of this type dilute acid be added, salt formation for which the dimethylamino-group is responsible (see formula I) takes place, with addition of one molecule of acid :

- I. $(\text{CH}_3)_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{N}\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$.
- II. $\text{HCl}(\text{CH}_3)_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{N}\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$.
- III. $\text{Cl}(\text{CH}_3)_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$.
- IV. $\text{ClH}(\text{CH}_3)_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{N}:\text{C}_{10}\text{H}_6\cdot\text{O} < \begin{matrix} \text{H} \\ \text{Cl} \end{matrix}$.

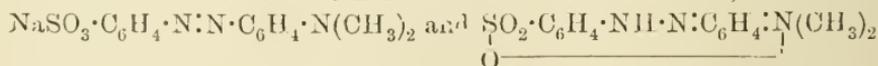
but whether the resulting salt is non-quinonoid (II) or quinonoid (III) was not investigated at the time. An excess of a strong acid involved the formation of a di-acid salt, and the explanation of this fact, as well as the great deepening in colour, was referred to oxonium salt formation (see formula IV above and table p. 338, *loc. cit.*), several di-acid salts being isolated and analysed.

Shortly after the publication of this work, it struck one of the authors as a virtual certainty that if the relationship of benzeneazophenol to its hydrochloride was to be represented by the formulæ



then, similarly, aminoazobenzene and its hydrochloride would possess the corresponding constitutions :

$\text{C}_6\text{H}_5\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ and $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{N}:\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{HCl}$,
so giving a reasonable explanation for the marked colour change produced on the conversion of the base into a salt. The application of this view to the case of the indicator methyl-orange (Hewitt, *Analyst*, 1908, 33, 85) leads one to the result that the sodium salt and the "free acid" or internal salt have the constitutions,

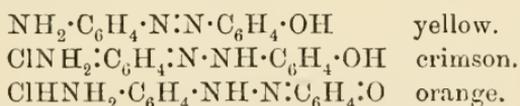


O

respectively; the same formulæ were published shortly afterwards by Hantzsch and Hilscher (*Ber.*, 1908, 41, 1171). In some discussion as to priority which followed (Hewitt, *Ber.*, 1908, 41, 1986; Hantzsch, *ibid.*, 2435), Fox published the interesting experimental fact that methyl-orange is readily decomposed by warm dilute nitric acid with production of diazobenzenesulphonic acid and 2:4-dinitromonomethylaniline, one of the methyl groups being eliminated in the reaction (*Ber.*, 1908, 41, 1989). This result is certainly in better agreement with a quinonoid structure for the "free acid" than a structure involving an unaltered azo-group.

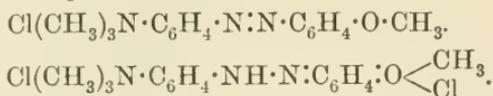
Whilst the work published last year will probably convince most persons intimately acquainted with azo-compounds of the quinonoid structure of the salts of the amino-derivatives, it appeared worth while to examine a case in which both aromatic nuclei were benzenoid, both on account of greater simplicity and to avoid the possible objection that the simplest case had not been examined and might possibly give different results to those obtained with naphthalene derivatives.

The expectation was that aminobenzeneazophenol, which has already been examined at some length by Meldola (*Trans.*, 1885, 47, 659), whilst giving yellow solutions in neutral solvents, would furnish solutions similar to that of acidified methyl-orange in presence of a medium amount of mineral acid, but that in concentrated mineral acids the colour would be comparable with that given by benzeneazophenol, the structures of the substance and its mono- and di-acid salts being represented by the constitutions:

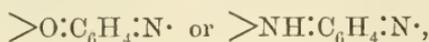


This expectation was fully confirmed by experiment, and the probability of the constitutions assigned to the respective substances received ample verification by the examination of the alkyl derivatives. The same colour changes were observed when the hydrogen atoms of the amino-group alone or of that and the hydroxyl group were replaced by methyl; obviously from the formulæ no radical difference is to be expected. But when hydroxy- or *p*-methoxy-benzeneazodimethylaniline was converted into a methiodide, whilst the colour of the salt in neutral solution was yellow, addition of hydrochloric acid produced no crimson shade, although if the acid were sufficiently concentrated the orange colour, associated in this case with oxonium salt formation, made itself manifest. A consideration of mono- and di-acid salts in this case shows the impossibility of the development of the quinonoid configuration with respect to that benzene nucleus to which the amino-

group is attached, whilst no inhibition of possible quinonoid structure has occurred with respect to the other nucleus :



Two points observed with regard to the photographs are well worth mention. The general type of quinonoid salt absorption is much the same whether the quinonoid grouping is of the type



but when the grouping is conditioned by double linking between carbon and nitrogen the oscillation frequency is less than when it is between carbon and oxygen. Ordinary chemical experience leads one to the conclusion that the linking C:N is weaker than C:O, and this would necessarily condition a slower rate of vibration.

p-Acetylaminobenzeneazophenol.

In the preparation of *p*-aminobenzeneazophenol we decided to use *p*-aminoacetanilide as starting point. This was dissolved in a little more than two molecular proportions of dilute hydrochloric acid (2 vols. of fuming acid to 5 vols. of water), diazotised with the calculated amount of sodium nitrite, and coupled with phenol in the presence of sodium carbonate. After acidification, collection, and crystallisation from dilute alcohol (equal volumes alcohol and water) the compound was obtained in beautiful reddish-brown plates melting at 198° (uncorr.) :

0.2183 gave 0.5272 CO₂ and 0.1011 H₂O. C = 65.9 ; H = 5.1.

C₁₄H₁₃O₂N₂ requires C = 65.9 ; H = 5.1 per cent.

p-Aminobenzeneazophenol.

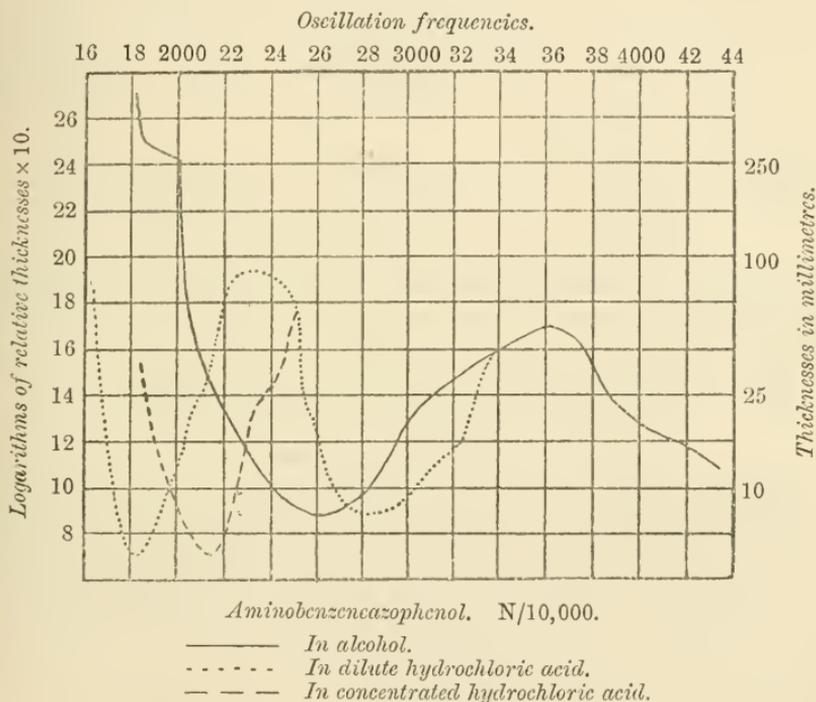
The acetyl derivative was hydrolysed by boiling for two to three hours with 20 parts of 20 per cent. hydrochloric acid. The magenta-coloured solution on neutralisation with sodium carbonate gave a precipitate of the amino-compound amounting to about 70 per cent. of the weight of the material taken. In the crude condition this melted at 177° (uncorr.) ; after crystallisation melting points of about 185° were observed. Meldola (*loc. cit.*) gives 181° ; no weight can be laid on a difference of a few degrees in these cases, as most of the substances examined decompose at the melting point, and the temperature observed necessarily depends on the rate of heating :

0.1038 gave 17.2 c.c. N₂ at 18° and 772 mm. N = 19.5.

C₁₂H₁₁ON₂ requires N = 19.7 per cent.

The substance gives yellow solutions in neutral solvents ; addition of dilute hydrochloric acid produces a magenta shade, but if concentrated hydrochloric acid be employed in excess, the solution becomes orange, owing to the production of di-acid salts. As Meldola has already isolated a platinichloride in which the azo-compound behaves as a mono-acid base, it was unnecessary for us to prepare any salts of this type, but on passing dry hydrogen chloride through a benzene solution of the base, a dark red precipitate was obtained, which was rapidly

FIG. 1.



collected, washed with benzene and light petroleum, and dried over sulphuric acid. This proved to be the di-acid salt :

0.1651 gave 0.3047 CO_2 and 0.0732 H_2O . C = 50.3 ; H = 4.9.

0.1545 ,, 0.1501 AgCl. HCl = 24.7.

$\text{C}_{12}\text{H}_{13}\text{ON}_3 \cdot 2\text{HCl}$ requires C = 50.3 ; H = 4.5 ; HCl = 25.5 per cent.

Fig. 1 gives the absorption spectra observed in the case of *p*-aminobenzeneazophenol without and with hydrochloric acid.*

p-Dimethylaminobenzeneazophenol.

The process adopted by Fox and Hewitt (*loc. cit.*), which consisted in diazotising *p*-phenylenedimethyldiamine and coupling with alkaline

* The curve for the dihydrochloride is not complete, as we suspected some hydrolysis, even with a large excess of hydrochloric acid present.

α -naphthol, proved unsuitable in this case. The diazonium salt is extremely unstable, and phenol does not couple so rapidly as α -naphthol, so that very little except tarry decomposition products was obtained.

5.45 Grams of *p*-aminophenol dissolved in 12 c.c. of concentrated hydrochloric acid and 25 c.c. of water were diazotised with 3.5 grams of sodium nitrite dissolved in 10 c.c. of water, and the solution added to 6.05 grams of dimethylaniline dissolved in 50 c.c. of glacial acetic acid mixed with ice and water in which sodium acetate had been dissolved in sufficient quantity. After keeping overnight, excess of water was added, and the precipitated azo-compound collected. The best yield obtained was 6.5 grams of crude product. On crystallisation from alcohol, bright red leaflets were obtained, melting and decomposing at 203—204°:

0.1568 gave 0.3991 CO₂ and 0.0875 H₂O. C = 69.4; H = 6.2.

0.1248 „ 0.3189 CO₂ „ 0.0714 H₂O. C = 69.7; H = 6.4.

C₁₄H₁₅ON₃ requires C = 69.7; H = 6.2 per cent.

The solution in dilute hydrochloric acid is magenta in colour, and yields a dark-coloured monohydrochloride on evaporation:

0.1411 gave 0.0724 AgCl. HCl = 13.3.

C₁₄H₁₅ON₃.HCl requires HCl = 13.2 per cent.

p-Dimethylaminobenzeneazophenyl Acetate.

Acetylation of the phenol was effected by three and a-half hours' boiling with its own weight of fused sodium acetate and four times its weight of acetic anhydride. Excess of acetic anhydride was destroyed by pouring into alcohol, and the substance was precipitated by the addition of water. When crystallised from alcohol, the substance was obtained in brown plates melting at 137° (uncorr.):

0.1376 gave 0.3402 CO₂ and 0.0747 H₂O. C = 67.4; H = 6.0.

C₁₆H₁₇O₂N₃ requires C = 67.8; H = 6.0 per cent.

p-Dimethylaminobenzeneazophenol Methiodide.

The dimethylamino-compound was heated for four hours at 100° with its own weight of dimethyl sulphate. The product was dissolved in hot water, filtered, and treated with an excess of potassium iodide, the iodide of the base separating on cooling. This was collected and obtained in black scales by crystallisation from alcohol:

0.1427 gave 13.5 c.c. N₂ at 19° and 769 mm. N = 11.2.

C₁₅H₁₅ON₃I requires N = 11.0 per cent.

As previously mentioned, this salt dissolves in water with a yellow colour, strongly contrasting with the isomeric salt of *p*-methoxybenzeneazodimethylaniline; this yellow colour is not affected by

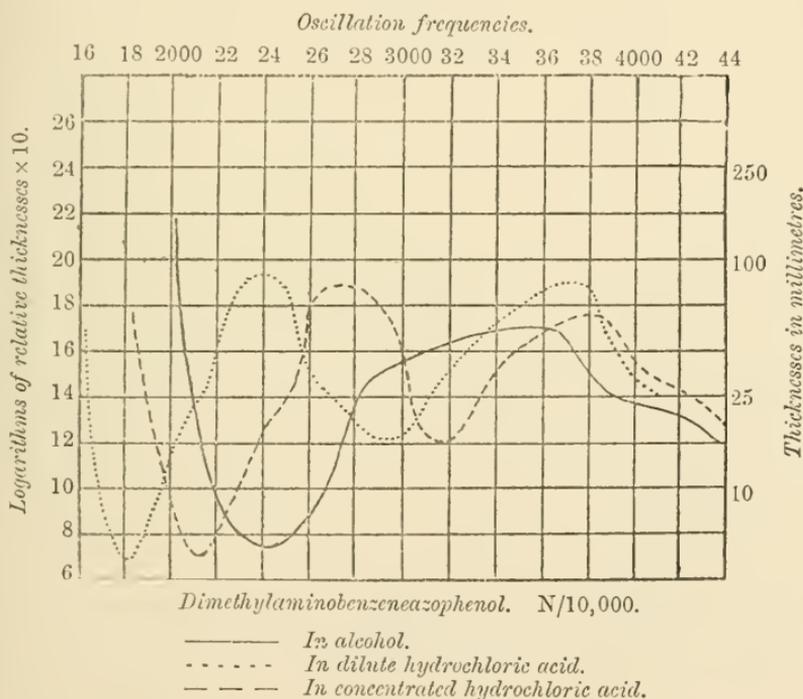
dilute acids, but gives place to an orange shade on formation of oxonium di-acid salts.

The absorption spectra of dimethylaminobenzeneazophenol are given in Fig. 2.

p-Methoxybenzeneazodimethylaniline.

6.15 Grams of *p*-anisidine dissolved in 16 c.c. of concentrated hydrochloric acid and 30 c.c. of water were diazotised by the addition of a solution of 3.5 grams of sodium nitrite, ice being added to the solution. The diazonium salt was then added to 6.05 grams of dimethylaniline emulsified with 30 c.c. of glacial acetic acid, 8 grams of

FIG. 2.



crystallised sodium acetate, and much ice. After seventeen hours the product was collected, washed, and crystallised. Using pyridine as solvent, brilliant orange prisms melting at 161° (uncorr.) are obtained, but from alcohol brown (almost bronze-coloured) plates and needles are deposited. The appearance of the two preparations is quite distinct, but no claim is made for the existence of two modifications, as both specimens alone and mixed show the same melting point:

0.1155 gave 16.1 c.c. N_2 at 14° and 772 mm. $N = 16.6$.

$C_{15}H_{17}ON_3$ requires $N = 16.5$ per cent.

The solutions in neutral solvents are yellow, in dilute acids magenta (almost violet), and orange in concentrated acids.

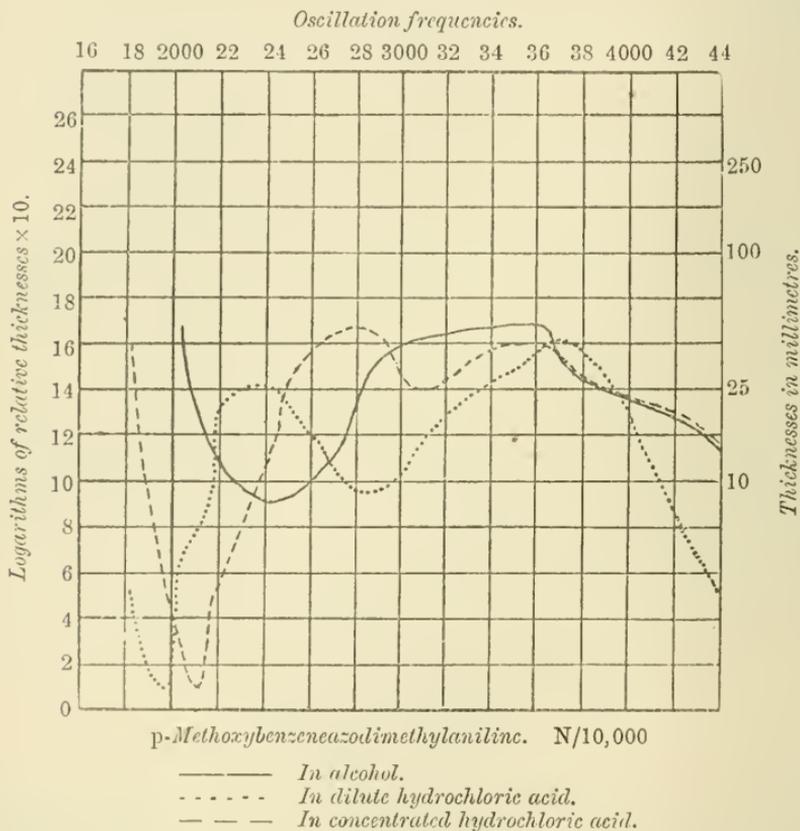
p-Methoxybenzeneazodimethylaniline Methiodide.

This was prepared in a similar manner to the corresponding phenolic derivative :

0.1524 gave 13.8 c.c. N_2 at 25° and 770 mm. $N = 10.4$.

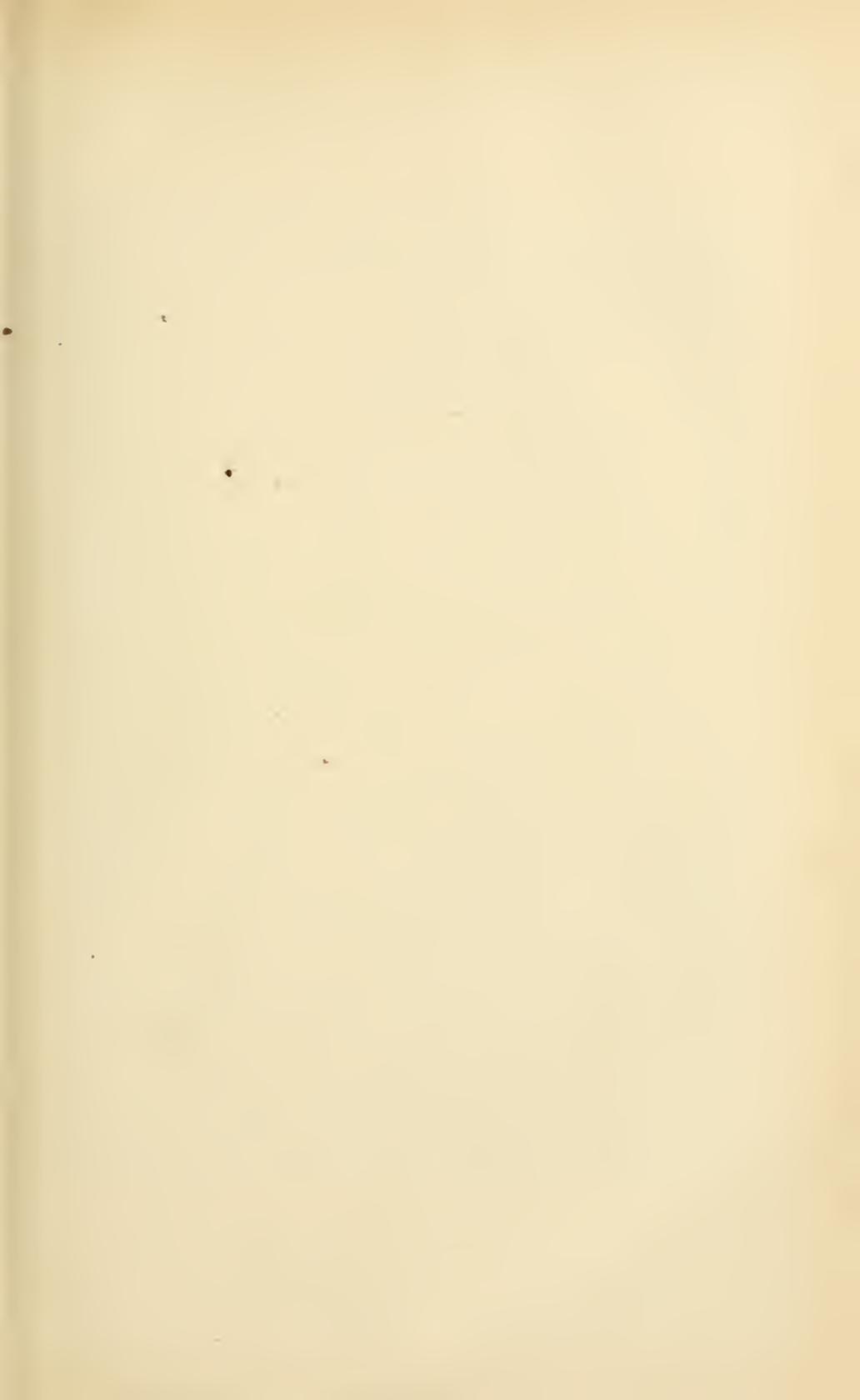
$C_{16}H_{20}ON_3I$ requires $N = 10.6$ per cent.

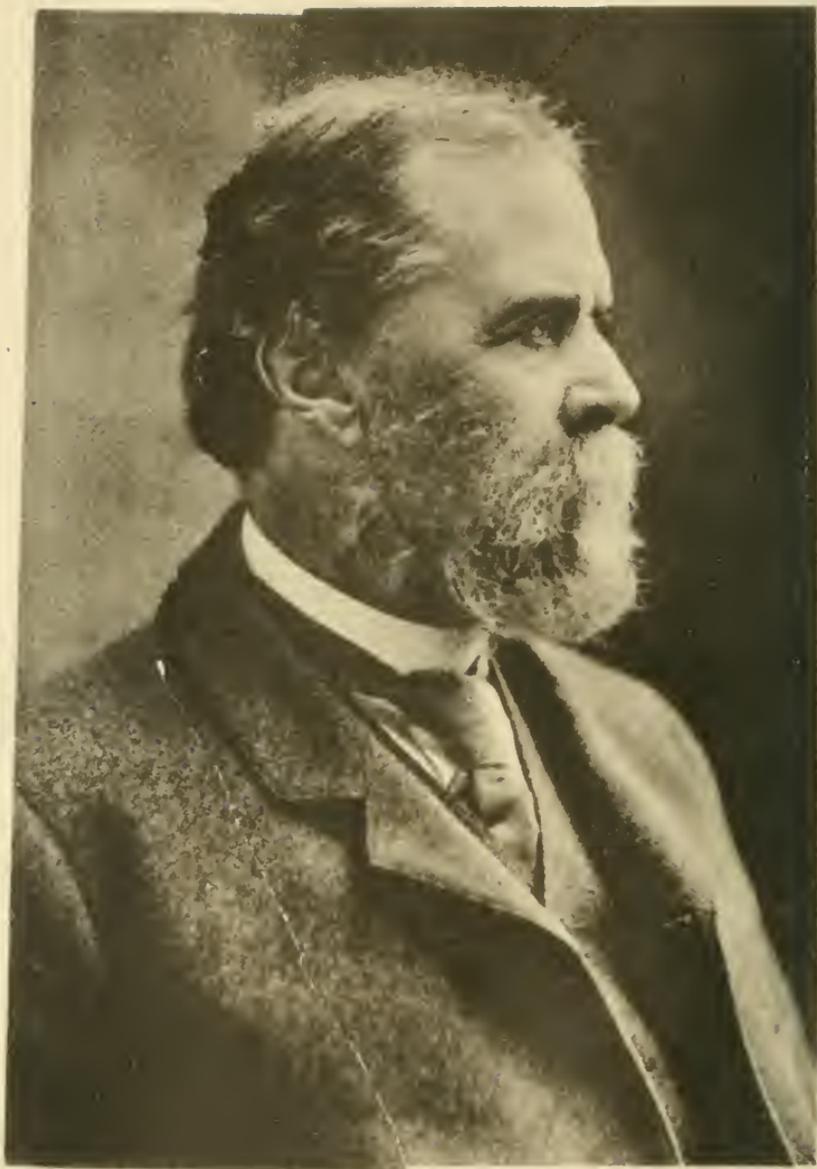
FIG. 3.



The aqueous solution is yellow, remains unaffected by dilute acids, but gives an orange shade with concentrated hydrochloric acid.

In conclusion, we wish to tender our thanks to the Government Grant Committee of the Royal Society for a grant by which part of the expenses of this investigation have been defrayed, and to Miss C. H. Watts for assistance with the photographic portion of the work.





WOLCOTT GIBBS MEMORIAL LECTURE.

DELIVERED ON JUNE 3RD, 1909.

By FRANK WIGGLESWORTH CLARKE.

It is easy to write biography when one is satisfied with a mere chronicle of events. But to clothe the skeleton of fact with flesh and blood, so that the man shall, as it were, live again, is difficult, and yet, figuratively speaking, that seems to be the sort of task which you have set before me. What manner of man was Wolcott Gibbs? What influences helped to mould his character? What did he do, and under what conditions was his work accomplished? These are the questions which I must try to answer.

Oliver Wolcott Gibbs (he dropped the Oliver early in his career) was born in the city of New York, on February 21, 1822. His father, Colonel George Gibbs, was a man of some wealth, who owned a large country place at Sunswick, on Long Island, not far from the then small city. He was an enthusiastic mineralogist, and gathered a collection which, ultimately sold to Yale College, became the nucleus of the great cabinet since made famous by the labours of the two Danas, Brush, and Penfield. It was perhaps the control of the Gibbs collection which first led J. D. Dana to write his classical *System of Mineralogy*. Colonel Gibbs, after whom the mineral *gibbsite* was named, was himself the author of several memoirs upon mineralogical subjects, and his eldest son, also named George, achieved some reputation as a geologist and as a student of ethnology. Wolcott Gibbs was born into an atmosphere of scientific interests, and his early associations must have influenced his choice of a career. A taste for science ran in the family.

Laura Gibbs, the mother of Wolcott, came of distinguished ancestry. Her father, Oliver Wolcott, rose through various positions to that of Secretary of the United States Treasury, a post which he held during the latter part of Washington's administration and well into the administration following. He then became a Justice of the United States Circuit Court, and during the last ten years of his life he was Governor of the State of Connecticut. His father, another Oliver, was a magistrate, a major-general of militia, a member of Congress, and a signer of the American Declaration of Independence. He, too, was a Governor of Connecticut, and so also was his father, Roger Wolcott, the first noteworthy member of the line. In short, the ancestors of Wolcott Gibbs were people of far more than average

ability, who had the confidence and esteem of their fellow citizens, and were therefore entrusted with positions of high rank and responsibility. Even though there was no commanding genius among them, no man of world-wide fame, they at least left to their descendants a legacy of lofty examples, well worthy of emulation. We may differ in our opinions as to the significance of heredity; but we can recognise the fact that Gibbs received from his forbears a sound mind in a sound body, together with traditions of well-doing that could not be disregarded. A good ancestry is a good beginning for any man.

In his early environment Gibbs was also fortunate. Although he was only eleven years old when he lost his father, his mother survived for many years, and gave him the best of opportunities for healthy development. She was a woman of strong character and unusual ability, and her home became a centre in which the best intellectual society of New York was to be found. Her character, forceful, positive, patriotic, and public-spirited, was reflected in that of her son.

The early childhood of Wolcott Gibbs was largely spent at his father's estate of Sunswick, where, as he tells us in a brief autobiographical note, "he was often occupied with making volcanoes with such materials as he could obtain, and in searching the stone walls . . . for minerals, and the gardens and fields for flowers." At the age of seven he was sent to a private school in Boston, where he was under the care of a maiden aunt, whose sister had married the famous Unitarian divine, William Ellery Channing. The winters were passed in Boston, and the summers with the Channings at their country place near Newport, Rhode Island. Here again he was surrounded by choice influences, and saw many distinguished people. The reputation of Dr. Channing attracted many visitors, including more than a few from abroad, and the boy must have come to some extent in contact with them. Being but a child, he may not have understood or appreciated his opportunities, but his imagination could not have been entirely unaffected. His early associations foreshadowed his later career.

When he was twelve years old, Gibbs returned to New York, and began his preparation for college. In 1837 he entered Columbia College as a freshman, and graduated in 1841. It was in his junior year that he published his first scientific paper, a description of a new form of galvanic battery, in which carbon was used, probably for the first time, as the inactive plate. This achievement, unimportant as it may seem now, was really remarkable in two ways; first, on account of the youth of the author, and, secondly, because of the conditions under which the work was

done. In those days the American colleges, like the public schools of England, were intensely classical in their aims, and science received the minimum of attention. Latin, Greek, and mathematics ruled the curriculum, with only a smattering of other subjects. Even in the classics literature was subordinate to grammar, and as for the modern languages they were almost, if not quite, ignored. What science was cultivated was taught by lectures and text-book recitations, for the era of laboratory instruction had not begun. That a pupil of eighteen should make an original investigation under such conditions was surprising, but it showed the irresistible tendencies at work in his mind. The early impulses, received from his father, could not be overcome.

After receiving his bachelor's degree, young Gibbs went to Philadelphia, where he served as assistant in the laboratory of Robert Hare, the well-known inventor of the compound blow-pipe, who was then Professor of Chemistry in the Medical School of the University of Pennsylvania. Gibbs's purpose was to fit himself for holding a similar professorship, and so, after several months of experience with Hare, he entered the College of Physicians and Surgeons in New York, and in 1845 became a full-fledged Doctor of Medicine. He never practised, and probably never intended to do so, for the study of chemistry was the main purpose of his life, and his medical studies were only a means to an end. Indeed, they stood him in good stead when, many years later, he undertook to study the physiological effects of isomeric organic substances on animals.

Up to this point the training of the future chemist had been only preliminary, a laying of foundations, so to speak. In his time advanced scientific education was not easily obtained in America, and ambitious students who were able to do so sought their higher opportunities in Germany. Accordingly, Doctor Gibbs, as we must now call him, went abroad, and began by spending several months with Rammelsberg in Berlin. After this he studied for a year under Heinrich Rose, which was followed by a semester with Liebig at Giessen. He next went to Paris, where he attended lectures by Laurent, Dumas, and Regnault, and in 1848 he returned home, ready to begin the real labours of his life. Among his teachers the one who most impressed him was Rose, whom Gibbs greatly admired, and who doubtless gave his pupil his strong bias towards analytical and inorganic chemistry. From his other teachers, however, Gibbs acquired a breadth of view and an insight into different fields of research, which made him all the stronger as an investigator. He was a chemist in the largest sense of the term, and not a mere sub-specialist.

After returning to America, Gibbs first delivered a short course of lectures at a small college in Delaware. Then, in 1849, his native city claimed his services, and he was appointed professor of chemistry in the newly established Free Academy, now the College of the City of New York. He remained in this position for fourteen years, chiefly occupied in teaching elementary students, and at first doing, apparently, little else. He was not idle by any means, but he was finding himself, and his time was not wasted. It was in 1857 that his first really notable research was given to the world, namely, the joint memoir of Gibbs and Genth on the ammonio-cobalt bases. Of this I shall speak more at length later. In 1851 he became an associate editor of the American Journal of Science, and began the preparation of a series of abstracts which brought the results of foreign investigations to the attention of American readers. These abstracts amounted in all to about 500 pages, and, despite their brevity, were conspicuously clear and comprehensive. In 1861 the first of his papers on the platinum metals appeared, and his reputation was at last firmly established.

Notwithstanding his recognised ability, Dr. Gibbs, during this period, suffered one serious disappointment. The chair of chemistry in his *alma mater*, Columbia College, became vacant, and Gibbs, backed by the recommendations of nearly all the leading men of science in America, was a candidate for the position. He was, however, a Unitarian, and Columbia was then an institution under sectarian control. Purely on religious grounds, his candidacy was rejected, and a man of far smaller attainments received the appointment. This was unfortunate for Columbia, but not altogether so for Gibbs. In 1863 he was called to a more desirable post, the Rumford Professorship in Harvard University. Nominally, this was a professorship of the "Application of Science to the Useful Arts," but its incumbent, in addition to lecturing on heat and light, was expected to take charge of the chemical laboratory in the Lawrence Scientific School, and this gave Gibbs a great opportunity for usefulness. Furthermore, the position was a delightful one on its social side, and he was thrown into close association with many congenial spirits. There were Louis Agassiz the zoologist, Asa Gray the botanist, Jeffries Wyman in comparative anatomy, Benjamin Pierce in mathematics, and J. P. Cooke in chemistry. Literature was represented by Longfellow, Lowell, Holmes, and other less famous writers; altogether an aggregation of distinguished men which could not be matched elsewhere in America, or equalled at few places in the world. Gibbs was among his peers, and in a place where his worth could be fully appreciated.

Dr. Gibbs remained in charge of the Scientific School laboratory for eight years, and during that time his researches were, for the great part, although not exclusively, devoted to analytical methods. The school was technically a department of Harvard University, and yet its work was carried on quite independently. The students were usually men of definite purposes, who knew what they wanted and went where it could be best obtained. They went to Agassiz for zoology, to Gray for botany, and to Gibbs for chemistry, because those men were the leaders in their respective subjects, and they worked, not in classes, but as individuals. The students in chemistry had little or nothing to do with the students in other branches, for the school was distinctly professional in its aims. Teachers from other institutions, seeking to enlarge their knowledge, were often among them. Gibbs was now training men who intended to become chemists, and some among them were qualified to assist in his investigations. Moreover, he was not overloaded by numbers, for he rarely had more than twenty students in attendance at any one time. There was one assistant, to relieve him of routine work; his lectures on light and heat cost him little effort, and he was therefore able to devote his energies to research more advantageously than ever before.

It was my good fortune to have been a student under Gibbs during the greater part of four years, from 1865 until 1869. I may therefore be permitted to speak of his teaching from my own experience, believing that in such matters the personal note is not without value. There was nothing unusual about the course of instruction so far as ordinary details went, for that necessarily followed certain well-established lines. Most of the students had already gained some elementary knowledge of chemistry; their work began with the usual practice in analytical methods and chemical manipulations, and as the men showed capacity they were admitted to the confidence of their master and aided him in his investigations. This procedure may seem commonplace enough to-day, but in the years of which I speak it was new to American institutions, and was looked upon doubtfully by some of the old-fashioned pedagogues. The students who chose to do so attended the excellent chemical lectures of Cooke in Harvard College, but that work was wholly optional. The only formal examination was the final examination for the bachelor's degree, and therefore there was no cramming for examinations. Gibbs apparently believed, although his belief was not stated in set terms, that a good teacher who kept in touch with his pupils should know perfectly well where they stood, and no examination could tell him anything more. In fact, examinations are often misleading, for the reason that even a fine scholar of nervous temperament may become confused

and helpless during the ordeal, and fail to answer the simplest questions. On the other hand, a poor student with a fair memory may cram for an examination, pass triumphantly, and amount to nothing afterwards. The real examinations under Gibbs were daily interviews, when he visited each student at his laboratory table and questioned him about his work. This, together with the reported analyses, gave the teacher a clear conception of the true standing of each man. The fewness of the pupils was a distinct advantage, for all worked together in one room, beginners and research students often side by side. The result was that they learned much from one another, and there were many discussions among them over the burning problems of the day. The men were taught to stand on their own feet, and to think for themselves, laying thereby a foundation for professional success which was pretty substantial. The course of instruction had no definite term of years prescribed for it, and graduation came whenever the individual had done the required amount of work and submitted an acceptable original thesis. The final examination was usually oral, each man alone with his master, and was conducted in an easy conversational way which tended to establish the confidence of the candidate from the very beginning. In my own case I remember that the questions covered a fairly broad range of chemical topics, and at the end of it Dr. Gibbs drew me into a sort of discussion or argument with him over the then modern doctrine of valency. I now see that his purpose was not merely to ascertain what I had read on the subject, but what I really thought about it, if indeed I was entitled to think at all. Gibbs invariably treated his students, not as so many vessels into which knowledge was to be poured, but as reasonable beings, with definite purposes, to whom his help must be given. That help was never denied to any man who showed himself at all worthy of it. The research work in which the advanced students shared, and for which they received public credit, served to teach them that chemistry was a living and growing subject, and to train them in the art of solving unsolved problems. They were taught to *do*, and encouraged to *think*, and if, on going forth into the world, they sometimes felt themselves qualified to revolutionise all science, their vanity did no harm and was soon remedied. An enlightened ignorance is only gained with advancing years, and the enthusiastic beginner cannot be expected to appreciate it. It is the last polish that the ripened scholar acquires.

What now is the meaning of this long disquisition upon the methods of Gibbs's laboratory? What was there at all unusual in his teaching? Nothing, perhaps, from a modern point of view,

but much that was new to America in the middle 'sixties. It was Gibbs's peculiar merit that he, more than any other one man, introduced into the United States the German conception of research as a means of chemical instruction, a conception which is now taken as a matter of course without thought of its origin. Gibbs worked with small resources and no help from outside; he was a reformer who never preached reform; his students rarely suspected that they were doing anything out of the ordinary; but they had the utmost confidence in their master, and took it for granted that his methods were sound. There was nothing of the drill master about Gibbs, no trace of pedantry, no ostentation of profound learning; but the students never doubted his sincerity of purpose and interest in their work, nor questioned his ability as a teacher. As for Gibbs himself, it is doubtful whether he ever imagined that his teaching was at all remarkable. He did what was to him the natural and obvious thing to do, simply and without pretence, and the results justified his policy. The success of his students is perhaps the best monument to his memory.

In 1871 the chemical instruction at Harvard University was reorganised, in spite of vigorous protests from Gibbs and many other leaders in science. The laboratory of the Scientific School was consolidated with that of the College, and Gibbs had no more students in chemistry. His work was limited to that of the Rumford professorship, a change which left him more time for personal research, but took from the students the inspiration of his teaching. The change may have been justifiable on grounds of economy, but it was otherwise a mistake, and it was so recognised among chemists generally. The economy was only financial; but an important asset of the University, the ability of a great teacher, was not turned to the best account. Fortunately for Gibbs, he had independent means, although he was not a rich man, and he was able to equip a small laboratory of his own and to employ a private assistant. In that laboratory he carried out those brilliant researches on the complex inorganic acids which marked the culmination of his career. The equipment was most modest, and in some respects it reminded one of the famous kitchen of Berzelius. Indeed, Gibbs's favourite piece of apparatus was that homely utensil, a cast-iron cooking stove, which served for several useful purposes. Precipitates could be dried in the oven, crucibles were buried in the coals, water was kept hot on top of it. As an instrument of research it was neither elegant nor orthodox, but it did the work, and what more could be desired? Gibbs adapted himself to circumstances, and cared little for the instrumental refinements which so many chemists seem to regard as necessary.

The real essentials were provided; mere conveniences, the luxuries of research, he could do without.

For sixteen years after the closing of the Scientific School laboratory, Dr. Gibbs lectured to small classes of students on the spectroscope and on thermodynamics. In 1887 he retired, as Professor-Emeritus, and went to live in his house at Newport, where he had been accustomed to spend his summer vacations. His private laboratory was moved to Newport also, and there he continued his investigations until, enfeebled by old age, he was obliged to rest on his laurels. As a recreation, he cultivated a flower garden, and was proudest of his roses. In that way his love of the beautiful found its chief expression. On December 9, 1908, he passed away, at the age of nearly eighty-seven. His wife, whose maiden name was Josephine Maura, and whom he had married in 1853, died several years earlier, leaving no children.

So much for biography. It now remains for us to consider the contributions of Gibbs to science, and to trace their relations, so far as may be practicable, to later work. An investigation never stands alone; each one touches other investigations at several points; and its worth may be greatest as the progenitor of later researches. The suggestiveness of a discovery, its influence in stimulating thought, is fully as important as its immediate outcome. It is a seed, whose value is finally determined by its fertility.

Gibbs's first paper, a "Description of a New Form of Magneto-Electric Machine, and an Account of a Carbon Battery of Considerable Energy," published when he was a junior student at Columbia, has already been mentioned. In 1844 he attempted to discuss the theory of compound salt radicles, and in 1847, while a student abroad, he published a number of mineral analyses. In 1850, Gibbs pointed out the interesting fact that compounds which change colour when heated do so in the direction of the red end of the spectrum. In 1852 he published the first of his memoirs upon analytical methods, in which he proposed the separation of manganese from zinc by means of lead peroxide; and in 1853 he prepared, and partly described, an arsenical derivative of valeric acid. In all of this work there was nothing of great importance, but its varied character is suggestive. It represents the efforts of an active mind, feeling its way under unfavourable conditions, and not quite sure of its true capacities. Mineral chemistry, organic chemistry, analytical chemistry, chemical theory, and physics, in turn attracted his attention during this formative period of his career. It was in the great research on the ammonio-cobalt bases that Gibbs finally found himself, and forced the world to recognise his ability. His apprenticeship was ended, and his work as a master had begun.

The first of the ammonio-cobalt compounds, the oxalate of luteocobalt, was prepared by Gmelin in 1822, the very year in which Gibbs was born. It was supposed, however, to be a salt of cobaltic acid, and several other chemists, who studied it later, shared in the same misapprehension. In 1847, Genth, then at Marburg, discovered other salts of these bases, but it was not until 1851, after his emigration to America, that he published his description of them in a rather obscure journal. Genth was the first to recognise the true character of the new compounds, and he was followed by Claudet and Fremy, the three chemists working independently of one another and almost simultaneously. Up to this point Fremy's work was the most exhaustive, but it left much to be desired.

Genth had identified the two bases since known as luteocobalt and roseocobalt. In 1852 Gibbs discovered the salts of xanthocobalt, which contained, in addition to the ammonia, a nitro-group. It was therefore quite natural that the two chemists should join forces, and in 1856 their celebrated memoir appeared. In this memoir thirty-five salts of the four bases roseocobalt, purpureocobalt, luteocobalt, and xanthocobalt were described, with adequate analyses, and, in eleven cases, crystallographic measurements by J. D. Dana. The roseo- and purpureo-compounds were for the first time clearly discriminated, although they were supposed to be isomeric, a misconception which could hardly have been avoided at that time. There was also an elaborate theoretical discussion on the constitution of the bases, but that also was premature. The fundamental theories of structure were yet to be developed. Blomstrand, Jörgensen, and Werner, in later years, utilised the data of Gibbs and Genth, and Werner especially made the ammonio-cobalt compounds the base of his famous theory of the constitution of the metal-amines. Gibbs and Genth laid the foundations, on which later investigators have built an imposing structure.

Gibbs was an experimentalist rather than a theorist, and yet he neither underrated nor avoided theory. In 1867 he published a paper on atomicities, or valences as they are now called, in which he developed the idea, then vaguely held by others, of residual affinities. He argued in favour of the quadrivalency of oxygen, and showed that on that supposition a molecule of water must be bivalent, and any chain of water molecules would be bivalent also. He then considered ammonia in the same way, with the two bonds of quinquevalent nitrogen unsatisfied. Ammonia, therefore, was weakly bivalent, and so, too, would be a chain of ammonia molecules. This conception he applied to the interpretation of the ammonio-cobalt bases, and so, too, did Blomstrand two years later. If we consider theories of this kind, not as finalities, but as attempts

to express known relations in symbolic forms, we must admit that Gibbs's conception was useful, and served well for the time being. That it has given way to other views more in harmony with modern discoveries, is not at all to the discredit of its author. In the later papers by Gibbs, published in 1875 and 1876, he made good use of his hypotheses, and described many more ammonio-cobalt compounds. Among them were the salts of an entirely new base, croceocobalt, in which two nitro-groups were present. In all, five distinct series were studied, their chlorides being represented, in modern notation, by the subjoined formulæ:

Luteocobalt chloride,	$\text{Co}(\text{NH}_3)_6\text{Cl}_3$.
Roseocobalt chloride,	$\text{Co}(\text{NH}_3)_5 \cdot \text{H}_2\text{O} \cdot \text{Cl}_3$.
Purpureocobalt chloride,	$\text{Co}(\text{NH}_3)_5 \cdot \text{Cl} \cdot \text{Cl}_2$.
Xanthocobalt chloride,	$\text{Co}(\text{NH}_3)_5 \cdot \text{NO}_2 \cdot \text{Cl}_2$.
Croceocobalt chloride,	$\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2 \cdot \text{Cl}$.

Gibbs's formulæ were somewhat different from these, being doubled, and with the water of roseocobalt regarded not as constitutional, but as crystalline. The simpler, halved expressions were established by cryoscopic methods which did not exist when Gibbs conducted his investigations.

The researches on the platinum metals, published by Gibbs in the years 1861 to 1864, relate mainly to analytical methods. Processes for the solution of iridosmine were carefully studied, and various new separations of the several metals from one another were devised. Incidentally, a number of new compounds were prepared, which, with a few exceptions, Gibbs never fully described. In 1871, however, he published a brief note on the remarkable complex nitrites formed by iridium, and in 1881 he described a new base, osmyl-ditetramine, $\text{OsO}_2 \cdot 4\text{NH}_3$, together with several of its salts. These researches were never pushed very far, and were discontinued for lack of proper facilities. They were, nevertheless, distinct additions to our knowledge of the platinum group.

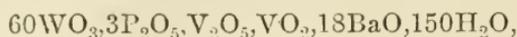
I have already mentioned the work done by Gibbs and his students in the laboratory of the Lawrence Scientific School. This covered a wide range, partly in developing and perfecting old analytical methods, partly in devising new ones. There were improvements in gas analysis, especially in the determination of nitrogen, and a great variety of analytical separations. I will not attempt to give a catalogue of these investigations, but will limit myself to a few of the more noteworthy. A new volumetric method for analysing the salts of heavy metals was worked out, in which a metal such as copper or lead was precipitated as sulphide, the acid being afterwards determined by titration. The estimation of

manganese as pyrophosphate was another of these contributions to analysis. But the most important of all was the electrolytic determination of copper, now universally used, which was first published from Gibbs's laboratory. It is true that a German chemist, Luckow, claimed to have used the method much earlier, but so far as I can discover he failed to publish it. Gibbs, therefore, is entitled to full credit for a process which was the progenitor of many others. The entire field of electrochemical analysis was thrown open by him, and it has been most profitably cultivated. Gibbs also, during this period of his activity, invented several instrumental devices of great convenience. The ring burner, and the use of porous septa when precipitates are to be heated in gases, are due to him. Furthermore, in co-operation with E. R. Taylor, he devised a glass and sand filter which was the forerunner of the porous cones invented by Munroe when the latter was a student in Gibbs's laboratory. That, in turn, preceded the well-known perforated crucibles of Gooch, who was one of Gibbs's assistants. The genealogy of these inventions is perfectly clear.

We come now to the remarkable series of researches on the complex inorganic acids, which Gibbs began to publish in 1877, and continued well into the 'nineties. The ground had already been broken by others; silicotungstates, phosphotungstates, phosphomolybdates, etc., were fairly well known, but they were commonly regarded as exceptional compounds rather than as representatives of a very general class. In his first, preliminary, communication upon the subject, Gibbs indicated the vastness of the field to be explored, and showed that the formation of complex acids was characteristic of tungsten and molybdenum to an extraordinary degree. The phenomena were general, not special; and no limit could be assigned to the possible number of acids which these elements might form.

In his systematic work, following his preliminary announcement, Gibbs first revised the sodium tungstates in order to determine their true composition. Then, after preparing a number of phosphotungstates and phosphomolybdates, he studied the corresponding compounds containing arsenic in place of phosphorus. He next obtained similar vanadium compounds, and also showed that the phosphoric oxide of the first known acids was replaceable by phosphorous and hypophosphorous groups. Later still, he replaced the normal phosphates by pyro- and meta-phosphates, and also prepared complex salts containing arsenious, antimonious, and antimonie radicles. Stanno-phosphotungstates and molybdates, platinotungstates, and complex acids containing mixed groups were discovered, together with analogous compounds of selenium,

tellurium, cerium, and uranium. One salt described, a phospho-vanadio-vanadico-tungstate of barium, had the formula



with a molecular weight of 20066. Compared with this substance, the supposed complexity of most organic compounds becomes simplicity itself, and their interpretation seems relatively like child's play. In all, Gibbs described complex salts belonging to more than fifty distinct series, and did his work in a small private laboratory with only a single assistant. With greater resources at his command, what might he not have accomplished?

In 1898, in his address as retiring president of the American Association for the Advancement of Science, Gibbs summed up his views as to the constitution of the complex acids. His presentation of the subject, however, can hardly be regarded as final. The problems involved are too complicated to be easily solved, and much future investigation is needed in order to determine the true character of these extraordinary substances. Gibbs was a pioneer, breaking pathways into a tangled wilderness; but the ways are now open, and he who wills may follow. Possibly some of the compounds so far obtained were double salts; others may have been isomorphous mixtures; and in some instances phenomena of solid solution perhaps obscured the truth. By physical methods, cryoscopic or ebullioscopic, the molecular weights of the salts must be determined; their ionisation needs to be studied, and in such ways their true nature can be ascertained. These methods of research have been mainly developed since the work of Gibbs was done; he, therefore, cannot be criticised for not employing them. Since his time chemists have come to recognise many compounds as salts containing complex ions, such as, for example, the oxalates, tartrates, etc., of iron, aluminium, chromium, and antimony with other bases of lower valency. Even many of the silicates are easiest to interpret as salts of alumino-silicic acids, although the physical proof of their nature is difficult to obtain. The constitution of the complex acids is one of the great outstanding problems of inorganic chemistry.

Although he was distinctively an inorganic chemist, Gibbs did not entirely neglect organic chemistry. In 1868 he discussed the constitution of uric acid and its derivatives, and in 1869 he described some products formed by the action of alkali nitrites on them. He also produced several memoirs on optical subjects, such as one on a normal map of the solar spectrum, and another on the wave-lengths of the elementary spectral lines. Again, he devoted some time to the study of interference phenomena, and discovered a constant, which he called the interferential constant,

that was independent of temperature. One of Gibbs's latest papers, published when he was seventy-one years old, related to that extremely difficult subject, the separation of the rare earths, a subject in which he had always taken a deep interest. In this paper he developed a new method for determining the atomic weights of the rare-earth metals, which was based upon analyses of their oxalates. The oxalic acid was determined by titration with permanganate solutions, and the oxides by ignition of the salts. From the ratios between the oxalic acid and the oxides, the molecular weights of the latter could be computed without reference to the amount of moisture in the initial substances. This method has since been employed by others, and especially by Brauner, in his work on the atomic weights of cerium and lanthanum. It is worth noting here that Gibbs had previously taken some part in atomic weight determinations. Those of Wing on cerium, and of Lee on cobalt and nickel, were made in Gibbs's laboratory and under his guidance. Furthermore, Gibbs was one of the earliest American chemists, if not the first, to accept the modern or Cannizzaro system of atomic weights, and to use it in his teaching. His mind was never closed to new ideas. It welcomed light from all sources.

Gibbs wrote no books and delivered no popular lectures. He was therefore little known to the public at large, but within scientific circles he received high honours. He was one of the founders of the National Academy of Sciences, and at one time its President, and he also presided over the American Association for the Advancement of Science. Honorary membership in the German, English, and American chemical societies, and in the Prussian Academy, was conferred upon him, and he received honorary degrees from several universities. His life was that of a devoted scholar, caring most for research, and indifferent to popularity. Sensationalism and self-advertising were most obnoxious to him; indeed, in these respects, no man could be more fastidious. The approval of his fellows he fully appreciated, but only when it was spontaneous and deserved. It must not be inferred from these remarks that Gibbs was deficient in public spirit, for that would be most untrue. During the Civil War, from 1861 to 1865, he was strongly patriotic, and did much to help the Union side. The Union League Club of New York, organised to bring together the more patriotic citizens of that city, was founded at a meeting in his house, and is to-day a strong social institution. Gibbs was also active in the Sanitary Commission, an organisation modelled upon the work of Florence Nightingale in the Crimea, and the forerunner of the Red Cross Society of to-day.

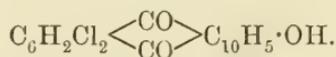
Wolcott Gibbs was a man of striking personality, tall, erect, and

dignified. As with most men of positive character, he had strong likes and dislikes, but the latter never assumed unworthy form. To his friends he was warmly devoted, and always ready to help them in their work with manifold suggestions. His breadth of mind is indicated by the range of his researches, and his liberality by the way in which he encouraged his students to develop his ideas. More than one important investigation was based upon hints received from him, and was carried out under his supervision, to appear later under another name. Gibbs never absorbed the credit due even in part to others, nor failed to recognise the merits of his assistants in the fullest way. Had he been more selfish, his list of publications would have lengthened; but his sense of justice was most keen, and therefore he held the esteem and confidence of his co-workers. No man, not even among his opponents, for such there were, could ever accuse him of unfairness. He deserved all honour, and his name will live long in the history of that science to which his life was given.

CXLV.—*Some Derivatives of Anthraquinone.*

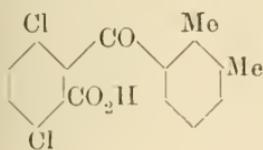
By DOROTHY HARROP, ROLAND VICTOR NORRIS, and CHARLES WEIZMANN.

IN a previous communication (this vol., p. 279) the authors have described certain derivatives of naphthacenequinone obtained by condensing 3:6-dichlorophthalic anhydride with α -naphthol by means of boric acid, the 3:6-dichloro-1'-hydroxy-2- β -naphthoylbenzoic acid being caused to undergo internal condensation by means of fuming sulphuric acid, producing 7:10-dichloro-1-hydroxynaphthacenequinone:

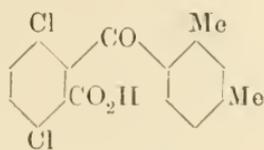


It was found that by boiling this quinone with aniline or toluidine, the chlorine atoms were replaced by the anilino- or toluidino-residues. In the present communication the authors have extended their investigations to the dimethylantraquinones, and find that the reactivity of the chlorine atoms is not restricted to amino-groups, but that phenol and thiophenol will react quite easily in presence of alkali, giving rise to the phenyl ethers of hydroxy- and thiol-antraquinones respectively. The dimethylantraquinones which are here described have been prepared in the usual way by condensing 3:6-dichlorophthalic anhydride with the three xylenes by means of

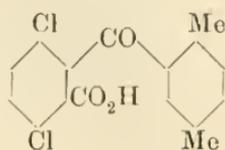
aluminium chloride, furnishing the corresponding dichlorodimethylbenzoylbenzoic acids in good yield.



(I.)

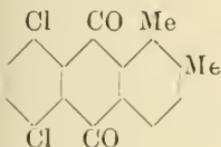


(II.)

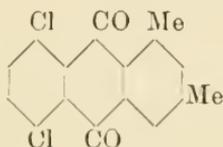


(III.)

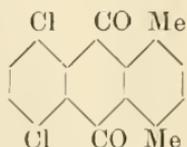
On bromination these acids form bromo-substituted derivatives, but only that derived from (II) has been isolated in the pure state. On warming the acids in fuming sulphuric acid in presence of boric acid, they yield the corresponding dichlorodimethylantraquinones.



(IV.)



(V.)



(VI.)

All these quinones crystallise well, and the yields are good except in the case of (V), where the closing of the ring is very difficult, and never more than 5 per cent. of the theoretical amount has been obtained. With fuming nitric acid all three quinones form nitro-derivatives; (V) and (VI) yield mononitro-compounds, but in the case of (IV) a dinitro-derivative is obtained.

As previously stated, when boiled with aniline in the presence of boric acid, or with phenol or thiophenol in the presence of alkali, each chlorine atom is displaced by the anilino-, phenoxy-, or phenylthiol group respectively. The dianilnodimethylantraquinones are dark blue, whilst the phenoxy- and phenylthiol derivatives are yellow and dark red respectively.

The entrance of the auxochromic groups into the anthraquinone molecule and their influence on the colour of the quinone follow the general rule. The position of the methyl groups exerts practically no influence on the colour of the compounds or on the colour of their solutions in concentrated sulphuric acid, except in the case of the phenoxy- and phenylthiol compounds. In the former case the quinone derived from *p*-xylene gives in sulphuric acid a much bluer shade of violet, whereas in the latter the reverse seems to hold good. The quinone derived from *p*-xylene gives a green coloration in concentrated sulphuric acid, whereas that from *o*-xylene gives a blue solution. The quinone from *m*-xylene also forms a blue solution, but turns green on gentle warming. The influence of the auxochromes is shown in the following table.

Substance.	Colour.	Colour in sulphuric acid.
Dimethylantraquinones.....	Yellow	
Dichlorodimethylantraquinones	Greenish-yellow	Orange-red
Dianilindimethylantraquinones	Blue	Green
Diphenoxydimethylantraquinones	Yellow	Violet
Diphenylthioldimethylantraquinones	Dark red	Blue

EXPERIMENTAL.

3 : 6-Dichloro-2' : 3'-dimethyl-2-benzoylbenzoic Acid (I, p. 1313).

This acid is prepared by condensing 3 : 6-dichlorophthalic anhydride and *o*-xylene in presence of aluminium chloride. One hundred grams of 2 : 6-dichlorophthalic anhydride, purified by distillation in a vacuum, are mixed with 150 grams of *o*-xylene, and 200 grams of finely powdered aluminium chloride are gradually added. The reaction soon becomes vigorous, and the mixture assumes a dark red colour. After the addition of the aluminium chloride, the whole is heated on the water-bath until hydrogen chloride is no longer evolved (four hours). The semi-solid mass is then decomposed by ice and dilute hydrochloric acid, and the excess of *o*-xylene is removed by distillation in a current of steam. The dark brown oil remaining slowly solidifies on cooling. It is purified by dissolving in dilute aqueous sodium hydroxide, warming with animal charcoal, and decomposing the alkaline solution by ice and hydrochloric acid, when dichlorodimethylbenzoylbenzoic acid separates as a bulky, grey precipitate. After collecting and drying, it is washed with cold benzene to remove traces of oily products, and finally purified by crystallisation from glacial acetic acid :

0.1141 gave 0.2478 CO₂ and 0.0402 H₂O. C = 59.21 ; H = 3.9.

0.1241 ,, 0.1089 AgCl. Cl = 21.72.

C₁₆H₁₂O₃Cl₂ requires C = 59.46 ; H = 3.72 ; Cl = 21.95 per cent.

3 : 6-Dichloro-2' : 3'-dimethyl-2-benzoylbenzoic acid when anhydrous melts at 181°. It is readily soluble in alcohol, and crystallises from glacial acetic acid in minute, colourless needles. Its sodium salt is yellow.

When its acetic acid solution is heated with a slight excess of bromine for twenty-four hours on the water-bath, a monobromo-derivative is produced, but so far this acid has not been obtained in a pure condition.

5 : 8-Dichloro-1 : 2-dimethylantraquinone (IV, p. 1313).

This is prepared by heating a mixture of the acid just described (50 grams), boric acid (50 grams), and an excess of fuming sulphuric acid, containing 10 per cent. of sulphur trioxide, to 120° for ten

minutes. The product is poured on ice, boiled, and filtered; the green precipitate of the quinone is freed from traces of acid by boiling with dilute aqueous sodium hydroxide, filtering, and then washing with a little dilute hydrochloric acid.

5 : 8-Dichloro-1 : 2-dimethylantraquinone crystallises from glacial acetic acid in greenish-yellow needles, which melt at 269—270° :

0.2454 gave 0.5643 CO₂ and 0.0785 H₂O. C = 62.71 ; H = 3.55.

0.1413 ,, 0.1317 AgCl. Cl = 23.04.

C₁₆H₁₀O₂Cl₂ requires C = 62.97 ; H = 3.28 ; Cl = 23.25 per cent.

This quinone is readily soluble in benzene or xylene, but only sparingly so in alcohol. Its solution in sulphuric acid is orange-red. When warmed with fuming nitric acid for about fifteen minutes and then poured into water it yields a dinitro-compound.

5 : 8-Dichlorodinitro-1 : 2-dimethylantraquinone crystallises from glacial acetic acid in pale yellow needles, which melt at 226°. It is practically insoluble in alcohol or benzene, but readily so in xylene :

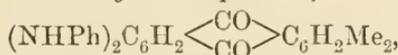
0.1085 gave 0.1926 CO₂ and 0.0216 H₂O. C = 48.40 ; H = 2.21.

0.1209 ,, 7.4 c.c. N₂ (moist) at 19° and 772 mm. N = 7.14.

0.1352 ,, 0.0958 AgCl. Cl = 17.52.

C₁₆H₈O₆N₂Cl₂ requires C = 48.61 ; H = 2.02 ; N = 7.09 ; Cl = 17.95 per cent.

5 : 8-Dianilino-1 : 2-dimethylantraquinone,



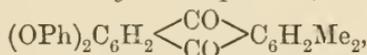
is formed when 5 : 8-dichloro-1 : 2-dimethylantraquinone, together with a little boric acid, is boiled with aniline for twelve hours. The original red solution gradually changes to blue. The solution is then treated with alcohol and hydrochloric acid, the precipitate collected, washed free from aniline hydrochloride, and crystallised from xylene, from which it separates in dark blue crystals. It is readily soluble in benzene, xylene, or nitrobenzene. Its solution in concentrated sulphuric acid is green :

0.1003 gave 0.2949 CO₂ and 0.0501 H₂O. C = 80.18 ; H = 6.61.

0.1106 ,, 6.4 c.c. N₂ (moist) at 20° and 757 mm. N = 6.61.

C₂₈H₂₂O₂N₂ requires C = 80.38 ; H = 5.26 ; N = 6.69 per cent.

5 : 8-Diphenoxy-1 : 2-dimethylantraquinone,



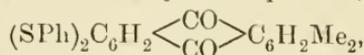
is prepared by boiling 10 grams of 5 : 8-dichloro-1 : 2-dimethylantraquinone with 10 grams of sodium hydroxide and a large excess of phenol for twenty minutes. The liquid, which has an orange-yellow colour, is acidified with hydrochloric acid, and the excess of phenol removed by distillation in a current of steam, when the diphenoxy-

quinone is left as a brown oil, which solidifies on cooling. After drying, it is purified by crystallisation from glacial acetic acid, from which it separates in yellow needles melting at 214° . It is readily soluble in benzene, xylene, or nitrobenzene, but sparingly so in alcohol. In concentrated sulphuric acid its solution possesses a fine violet colour, which becomes redder on the addition of fuming sulphuric acid:

0.1243 gave 0.3643 CO_2 and 0.0532 H_2O . C = 79.89; H = 4.76.

$\text{C}_{28}\text{H}_{20}\text{O}_4$ requires C = 80.00; H = 4.76 per cent.

5 : 8-Diphenylthiol-1 : 2-dimethylantraquinone,



is prepared in an exactly similar manner to the above-mentioned phenoxy-derivative, replacing the phenol by thiophenol:

0.1442 gave 0.3912 CO_2 and 0.0539 H_2O . C = 74.00; H = 4.31.

0.2013 ,, 0.2113 BaSO_4 . S = 14.41.

$\text{C}_{28}\text{H}_{20}\text{O}_2\text{S}_2$ requires C = 74.33; H = 4.42; S = 14.15 per cent.

5 : 8-Diphenylthiol-1 : 2-dimethylantraquinone crystallises from acetic acid in beautiful dark red needles, is readily soluble in xylene or nitrobenzene, but only slightly so in alcohol. Its solution in concentrated sulphuric acid is dark blue.

3 : 6-Dichloro-2' : 4'-dimethyl-2-benzoylbenzoic Acid (II, p. 1313).

This acid is prepared by condensing 3 : 6-dichlorophthalic anhydride with *m*-xylene in presence of aluminium chloride as described in the preparation of 3 : 6-dichloro-2' : 3'-dimethyl-2-benzoylbenzoic acid (p. 1314), which acid it resembles in properties. It melts at 164° :

0.1166 gave 0.2417 CO_2 and 0.0303 H_2O . C = 59.60; H = 3.64.

0.1462 ,, 0.1249 AgCl . Cl = 21.80.

$\text{C}_{16}\text{H}_{12}\text{O}_3\text{Cl}_2$ requires C = 59.46; H = 3.72; Cl = 21.95 per cent.

3 : 6-Dichloro-5'-bromo-2' : 4'-dimethyl-2-benzoylbenzoic acid is obtained when the acetic acid solution of the acid just described is heated on the water-bath with an excess of bromine for twenty hours.

On pouring the solution into water, a sticky, white precipitate is formed, which is collected, washed with sodium hydrogen sulphite, and crystallised from xylene:

0.1053 gave 0.1835 CO_2 and 0.0285 H_2O . C = 47.51; H = 3.00.

0.1343 ,, 0.1569 AgCl and AgBr . Cl + Br = 37.24.

$\text{C}_{16}\text{H}_{11}\text{O}_3\text{Cl}_2\text{Br}$ requires C = 47.77; H = 2.73; Cl + Br = 37.54 per cent.

3 : 6-Dichloro-5'-bromo-2' : 4'-dimethyl-2-benzoylbenzoic acid crystallises in small, colourless needles, which dissolve readily in alcohol, benzene, or xylene. Its sodium salt is yellow.

5 : 8-Dichloro-1 : 3-dimethylantraquinone (V, p. 1313).

This quinone is prepared in a similar manner to the quinone derived from *o*-xylene (p. 1314) by heating 3 : 6-dichloro-2' : 4'-dimethyl-2-benzoylbenzoic acid with boric acid and fuming sulphuric acid. The yield, however, is extremely poor, a large quantity of resinous matter being invariably formed. The best results are obtained by using sulphuric acid containing about 30 per cent. of sulphur trioxide, and keeping the temperature below 110°. It is also advisable to carry out the operation with very small quantities (5 grams) at a time. In no case, however, was the yield more than 5 per cent. The quinone is purified by crystallisation from acetic acid, from which it separates in pale greenish-yellow needles melting at 208°. Its properties are similar to those of the quinone derived from *o*-xylene (p. 1315) :

0·1249 gave 0·2879 CO₂ and 0·0392 H₂O. C = 62·86 ; H = 3·49.

0·1443 ,, 0·1349 AgCl. Cl = 23·11.

C₁₆H₁₀O₂Cl₂ requires C = 62·97 ; H = 3·28 ; Cl = 23·25 per cent.

On warming this compound with fuming nitric acid for fifteen minutes and pouring the solution into water, a mononitro-derivative is obtained.

5 : 8-Dichloronitro-1 : 3-dimethylantraquinone crystallises from acetic acid solution in yellow needles :

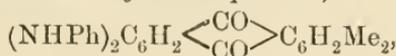
0·1102 gave 0·2198 CO₂ and 0·0237 H₂O. C = 54·4 ; H = 2·39.

0·0750 ,, 2·8 c.c. N₂ at 14° and 749 mm. N = 4·32.

0·1554 ,, 0·1264 AgCl. Cl = 20·12.

C₁₆H₉O₄NCl₂ requires C = 54·87 ; H = 2·57 ; N = 4·00 ; Cl = 20·26 per cent.

5 : 8-Dianilino-1 : 3-dimethylantraquinone,



is obtained by boiling aniline and 5 : 8-dichloro-1 : 3-dimethylantraquinone under the same conditions as those described previously (p. 1315). It crystallises from xylene in dark blue needles. When dissolved in concentrated sulphuric acid it forms a green solution :

0·1063 gave 0·3125 CO₂ and 0·0514 H₂O. C = 80·17 ; H = 5·37.

0·1241 ,, 7·2 c.c. N₂ at 20° and 758 mm. N = 6·62.

C₂₈H₂₂O₂N₂ requires C = 80·38 ; H = 5·26 ; N = 6·69 per cent.

5 : 8-Diphenoxy-1 : 3-dimethylantraquinone,



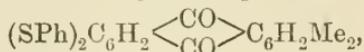
is prepared in exactly the same manner as 5 : 8-diphenoxy-1 : 2-dimethylantraquinone (p. 1315). It crystallises from acetic acid in yellow needles, which melt at 186° :

0.1336 gave 0.3904 CO₂ and 0.0558 H₂O. C = 79.69; H = 4.64.

C₂₈H₂₀O₄ requires C = 80.00; H = 4.76 per cent.

Its solution in concentrated sulphuric acid is reddish-violet.

5 : 8-Diphenylthiol-1 : 3-dimethylantraquinone,



is prepared by boiling thiophenol and 5 : 8-dichloro-1 : 3-dimethylantraquinone in presence of alkali (see p. 1316). It crystallises from acetic acid in dark red needles, which melt at 207°. Its solution in sulphuric acid is blue, but turns green on gentle warming :

0.1136 gave 0.3103 CO₂ and 0.0462 H₂O. C = 74.49; H = 4.52.

0.1879 „ 0.1961 BaSO₄. S = 14.32.

C₂₈H₂₀O₂S₂ requires C = 74.33; H = 4.42; S = 14.15 per cent.

3 : 6-Dichloro-2' : 5'-dimethyl-2-benzoylbenzoic Acid (III, p. 1313).

This acid is prepared by condensing 3 : 6-dichlorophthalic acid with *p*-xylene in presence of aluminium chloride (see p. 1314). It crystallises from acetic acid in colourless needles melting at 152° :

0.1458 gave 0.3182 CO₂ and 0.0514 H₂O. C = 59.52; H = 3.91.

0.1567 „ 0.1375 AgCl. Cl = 21.69.

C₁₆H₁₂O₃Cl₂ requires C = 59.46; H = 3.72; Cl = 21.95 per cent.

It forms a bromo-derivative on prolonged treatment with bromine in acetic acid solution, but, so far, this has not been obtained in a condition sufficiently pure for analysis.

5 : 8-Dichloro-1 : 4-dimethylantraquinone (VI, p. 1313).

This is obtained in almost quantitative yield by heating 3 : 6-dichloro-2' : 5'-dimethyl-2-benzoylbenzoic acid with concentrated sulphuric acid containing 10 per cent. of sulphur trioxide.

It crystallises from acetic acid in pale yellow needles melting at 244°. It has similar properties to the two dimethylantraquinones already described. Its solution in sulphuric acid is orange-red :

0.1064 gave 0.2449 CO₂ and 0.0333 H₂O. C = 62.75; H = 3.47.

0.1539 „ 0.1453 AgCl. Cl = 23.35.

C₁₆H₁₀O₂Cl₂ requires C = 62.97; H = 3.28; Cl = 23.25 per cent.

5 : 8-Dichloronitro-1 : 4-dimethylantraquinone is obtained by treating the above compound with fuming nitric acid. It crystallises from acetic acid in pale yellow needles melting at 243° :

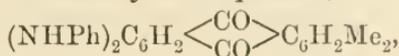
0.1156 gave 0.2321 CO₂ and 0.0259 H₂O. C = 54.75; H = 2.49.

0.0886 „ 3.0 c.c. N₂ at 19° and 764 mm. N = 3.91.

0.1663 gave 0.1348 AgCl. Cl = 20.04.

$C_{16}H_{19}O_4NCl_2$ requires C = 54.87; H = 2.57; N = 4.00; Cl = 20.26 per cent.

5 : 8-Dianilino-1 : 4-dimethylantraquinone,



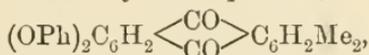
is prepared by boiling the corresponding dichloro-quinone with aniline in presence of boric acid (see p. 1315). It crystallises from xylene in dark blue needles, and forms a green solution in concentrated sulphuric acid :

0.1062 gave 0.3122 CO_2 and 0.0572 H_2O . C = 80.19; H = 5.35.

0.1503 ,, 8.8 c.c. N_2 at 19° and 765 mm. N = 6.65.

$C_{28}H_{22}O_2N_2$ requires C = 80.38; H = 5.26; N = 6.69 per cent.

5 : 8-Diphenoxy-1 : 4-dimethylantraquinone,

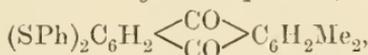


is prepared in the same way as the previously described diphenoxy-derivatives. It crystallises in yellow needles melting at 154° . Its solution in sulphuric acid is much bluer than the two previously mentioned diphenoxy-quinones :

0.1045 gave 0.3062 CO_2 and 0.0457 H_2O . C = 79.87; H = 4.86.

$C_{28}H_{20}O_4$ requires C = 80.00; H = 4.76 per cent.

5 : 8-Diphenylthiol-1 : 4-dimethylantraquinone,



prepared as described in the case of the corresponding compounds derived from *o*- and *m*-xylene (p. 1316), crystallises in dark red needles. Its solution in concentrated sulphuric acid is green :

0.1263 gave 0.3432 CO_2 and 0.0484 H_2O . C = 74.12; H = 4.24.

0.1661 ,, 0.1741 $BaSO_4$. S = 14.38.

$C_{28}H_{20}O_2S_2$ requires C = 74.33; H = 4.42; S = 14.15 per cent.

THE UNIVERSITY,
MANCHESTER.

CXLVI.—The Colour and Constitution of Diazonium Salts. Part I.

By GILBERT T. MORGAN and MARY ALCOCK, B.Sc., A.R.C.S.

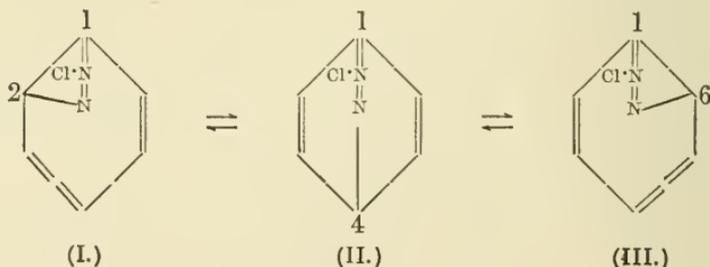
IN accordance with the hypothesis first put forward by Cain (Trans., 1907, 91, 1040), diazonium salts must be regarded as substances of a hemi-quinonoid type, and this view receives confirmation from the following circumstances: the fact that only aromatic amines can be

diazotised, the great reactivity of diazonium salts, the readiness with which these substances lose their diazo-nitrogen, and the not infrequent appearance of colour among this class of compounds.

The static para-configuration (II) for diazonium salts has, however, been adversely criticised by those who contend that substances having the second nitrogen atom attached to the para-carbon atom of the nucleus should yield para-diamines on reduction, a result which has not hitherto been observed. The connexion between the tervalent diazo-nitrogen and the para-carbon atom can, therefore, scarcely have the stability generally associated with a single linking.

This criticism is equally applicable to the ortho-quinonoid configuration (I and III) suggested as a possible alternative (Trans., 1907, 91, 1315), for such compounds should, in like manner, yield ortho-diamines.

This objection is met by the hypothesis put forward by one of the authors in conjunction with Miss Micklethwait, according to which these static ortho- and para-configurations may be regarded as successive phases in the life history of a diazonium salt. It is assumed that the direction of the third valency of the tervalent nitrogen atom undergoes a rhythmical change, so that it is directed successively towards the carbon atoms in positions 2, 4, and 6 in the nucleus* (Trans., 1908, 93, 618).



This conception of shifting valency directions has already afforded an explanation of the chemical reactions of compounds of very varied type. It forms an essential part of Kekulé's hypothesis of the constitution of benzene, and quite recently has been systematically employed under the name of "isorropesis" by Baly and his collaborators as a working hypothesis of the structure of compounds displaying certain spectroscopic peculiarities.

With the object of gaining further information as to the behaviour of diazonium derivatives, experiments have been made on benzoyl-

* This dynamic formulation can be readily illustrated by the simple mechanical models devised by Mr. A. Clayton to meet this case and also that of the oscillating bonds of the Kekulé formula for benzene.

p-phenylenediamine and its homologues, inasmuch as these bases furnish exceptionally stable diazonium salts.

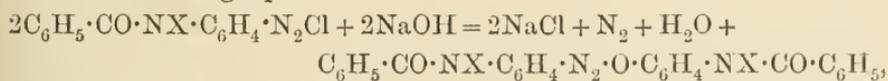
Benzoyl-*p*-aminobenzenediazonium hydroxide has already been shown to yield a nitrite and a carbonate (Trans., 1905, 87, 933), and in this research the *chloride*, *acetate*, and *perchlorate* have been shown to be stable in the dry state. The last of these is, therefore, remarkably different from benzenediazonium perchlorate, which is described as extremely explosive even in a moist condition (Vorländer, Ber., 1906, 39, 2715).

It might accordingly be supposed that the presence of the *p*-benzoylamino-group brings about a variation in the configuration of the diazonium complex, whereby a more stable molecule results. This structural variation could only be produced by a migration of the labile hydrogen atom from the benzoylamino-group, $C_6H_5 \cdot CO \cdot NH$, to the diazonium complex, leading to the formation of a salt having the following formula: $C_6H_5 \cdot CO \cdot N : C_6H_4 : N_2 \cdot HCl$.

This possibility is now quite excluded, because it has been shown that the bases in which this hydrogen is replaced by methyl and ethyl give rise to diazonium salts having the same chemical properties as those containing the group $C_6H_5 \cdot CO \cdot NH$.

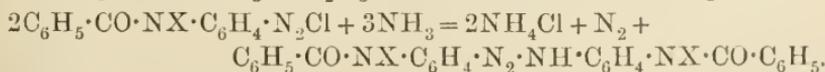
as-Benzoylmethyl-*p*-phenylenediamine and as-benzylethyl-*p*-phenylenediamine have been prepared and studied from this standpoint. These bases are more fusible than benzoyl-*p*-phenylenediamine, and a similar fall in the melting point is noticed in their corresponding derivatives. This difference is most pronounced in the case of the diazonium salts, for whereas the benzoyl-*p*-aminobenzenediazonium salts are crystallisable solids, the benzoylalkyl-*p*-aminobenzenediazonium salts, with few exceptions (for example, the molybdates and tungstates) are oily at the ordinary temperature. In other respects, these solid and oily diazonium salts are similar; they are colourless and stable when dry, and undergo similar transformations on treatment with alkalis.

Sodium hydroxide and these diazonium salts interact in accordance with the following equation:



where X = H, CH_3 , or C_2H_5 .

With ammonia the course of the change depends, to some extent, on the nature of the radicle X in the foregoing formula, for, when this symbol represents CH_3 or C_2H_5 , a diazoamine is the main product:



When X is hydrogen, the reaction leads partly to the diazoamine, but also to the diazo-oxide. The nitrogen eliminated in these decom-

positions is set free as such, and no trace of nitrite could be detected. These diazonium salts differ, therefore, from *p*-nitrobenzenediazonium chloride, which has recently been found to regenerate nitrite under treatment with alkalis (*Ber.*, 1909, 42, 881).

Summary.

These experiments show that the diazonium salts of benzoyl-*p*-phenylenediamine and the *as*-benzoylalkyl-*p*-phenylenediamines are similarly constituted, so that their stability must be attributed to the introduction into the nucleus of the heavy substituent $C_6H_5 \cdot CO \cdot NX$ (where X is H, CH_3 , or C_2H_5), and not to any modification of the ordinary diazonium configuration. When treated with aqueous sodium hydroxide and ammonia, these diazonium salts lose half their diazo-nitrogen, yielding diazo-oxides and diazoamines respectively.

EXPERIMENTAL

Preparation of the N-Alkyl Homologues of Benzoyl-p-phenylenediamine.

as-Benzoylmethyl-*p*-phenylenediamine, $COPh \cdot NMe \cdot C_6H_4 \cdot NH_2$.—Methyl-*p*-nitroaniline, obtained by methylating 4:4'-dinitrodiazaminobenzene and decomposing the resulting alkyldiazoamine with concentrated hydrochloric acid (Meldola and Streatfeild, *Trans.*, 1888, 53, 667), was benzoylated with benzoyl chloride in boiling toluene (compare Meldola and Salmon, *Trans.*, 1888, 53, 776), and the benzoylmethyl-*p*-nitroaniline thus produced was reduced with iron filings and very dilute hydrochloric acid, the following quantities being convenient proportions for this experiment: 12 grams of nitro-compound, 750 c.c. of water, 6 c.c. of concentrated hydrochloric acid, and 15 grams of iron filings. After one hour's heating, the mixture, rendered distinctly alkaline with sodium carbonate, was rapidly filtered while hot, and the residue of iron and iron oxide was repeatedly extracted with hot water. The diamine separated in colourless needles, the yield being about 87 per cent. When crystallised successively from toluene and light petroleum (b. p. 80–100°), the base, which is only very sparingly soluble in the latter solvent, melted at 153–154°:

0.1814 gave 0.4896 CO_2 and 0.1049 H_2O . C = 73.60; H = 6.43.

0.3349 „ 36.6 c.c. N_2 at 20° and 748.4 mm. N = 12.31.

$C_{14}H_{14}ON_2$ requires C = 74.33; H = 6.19; N = 12.39 per cent.

as-Benzylethyl-*p*-phenylenediamine, $COPh \cdot NEt \cdot C_6H_4 \cdot NH_2$.—Benzylethyl-*p*-nitroaniline, prepared by the method already employed for benzoylmethyl-*p*-nitroaniline, was also reduced in a similar manner.

The resulting base resembled the foregoing diamine, and was crystallised successively from water, benzene, and light petroleum; it then separated in colourless needles, and melted at 117° :

0.1577 gave 0.4372 CO_2 and 0.0956 H_2O . C = 75.61; H = 6.75.

0.2594 „ 26.3 c.c. N_2 at 23° and 773 mm. N = 11.66.

$\text{C}_{15}\text{H}_{16}\text{ON}_2$ requires C = 75.00; H = 6.67; N = 11.67 per cent.

as-Benzoylethyl-*p*-phenylenediamine and the foregoing base are very sensitive to the action of water or moist solvents, particularly in the presence of alkalis. In these circumstances they darken very perceptibly, this action taking place more readily in the presence of light. Benzoyl-*p*-phenylenediamine is itself oxidised with similar readiness, and the colourless preparations required for the following experiments were obtained by crystallisation from dry solvents, such as benzene, toluene, and light petroleum.

The Diazonium Salts of Benzoyl-p-phenylenediamine and its as-N-Alkyl Homologues.

Benzoyl-p-phenylenediamine hydrochloride, $\text{COPh}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2\cdot\text{HCl}$, is a white solid obtained by passing hydrogen chloride into a warm solution of the base in benzene or toluene:

0.3314 gave 0.1861 AgCl . Cl = 13.90.

$\text{C}_{13}\text{H}_{13}\text{ON}_2\text{Cl}$ requires Cl = 14.29 per cent.

This salt is insoluble in ether, but dissolves readily in alcohol or water. When diazotised with amyl nitrite in glacial acetic acid, ether precipitates *benzoyl-p-aminobenzenediazonium chloride*,



as a colourless, crystalline solid very soluble in water or alcohol, the aqueous solution having a neutral reaction to litmus:

0.2028 gave 0.1089 AgCl . Cl = 13.29.

$\text{C}_{13}\text{H}_{10}\text{ON}_3\text{Cl}$ requires Cl = 13.68 per cent.

The dry salt decomposes at about 139° , and when boiled in aqueous solution it evolves nitrogen and yields benzoyl-*p*-aminophenol (m. p. 206°). The corresponding diazonium nitrate obtained from this chloride and potassium nitrate by double decomposition separates in lustrous, colourless crystals.

Benzoyl-p-aminobenzenediazonium acetate, $\text{COPh}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{OAc}$, is obtained by diazotising with amyl nitrite a glacial acetic acid solution of benzoyl-*p*-phenylenediamine and precipitating with dry ether. As thus obtained the diazonium acetate is a colourless, crystalline substance, which turns yellow and then changes to brown on exposure to the atmosphere:

0.1181 gave 14.3 c.c. N_2 at 21° and 766.5 mm. $N = 13.91$.

$C_{15}H_{13}O_3N_3$ requires $N = 14.84$ per cent.

Benzoyl-p-aminobenzediazonium perchlorate, obtained from the diazonium chloride and potassium perchlorate in warm aqueous solution, crystallises on cooling in colourless needles, which turn yellow on exposure to light and air. This salt explodes on heating or on percussion:

Found, $N = 11.70$. $C_{13}H_{10}O_5N_3Cl$ requires $N = 12.98$ per cent.

Benzoyl-p-aminobenzediazonium sulphate, prepared in the same way as the chloride, is precipitated in colourless crystals by ether. The product appeared to be a mixture of normal and acid sulphates, the estimations of sulphur and nitrogen both giving numbers in accordance with this view.

The foregoing diazonium salts are all colourless when freshly prepared from pure benzoyl-*p*-phenylenediamine, but become coloured on exposure to the atmosphere. They couple readily with alkaline β -naphthol, giving rise to benzoyl-*p*-aminobenzeneazo- β -naphthol.

The diazonium chloride reacts with potassium chromate, potassium ferricyanide, and barium platinumocyanide, giving rise to yellow, crystalline, sparingly soluble diazonium salts. The diazonium tungstate and molybdate of benzoyl-*p*-phenylenediamine, unlike the corresponding salts of the *N*-methyl and *N*-ethyl bases, are very unstable, and cannot be preserved; the diazonium azide is a sparingly soluble, white substance, which rapidly evolves nitrogen.

Benzoyl-p-aminodiazobenzene cyanide, $COPh \cdot NH \cdot C_6H_4 \cdot N_2 \cdot CN$, produced by the interaction of molecular proportions of the diazonium chloride and potassium cyanide in aqueous solution, separates as an orange-coloured precipitate, which is quite stable on drying:

0.1823 gave 0.4457 CO_2 and 0.0792 H_2O . $C = 66.68$; $H = 4.52$.

0.2197 ,, 43.8 c.c. N_2 at 24.5° and 768 mm. $N = 22.55$.

$C_{14}H_{10}ON_4$ requires $C = 67.20$; $H = 4.00$; $N = 22.67$ per cent.

Only this modification of the diazo-cyanide could be obtained; it does not couple with alkaline β -naphthol.

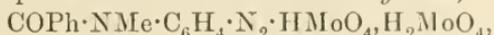
Diazonium Salts of the as-Benzoylalkyl-p-phenylenediamines.

The diazonium salts from *as*-benzoylmethyl-*p*-phenylenediamine and *as*-benzoylethyl-*p*-phenylenediamine and the commoner acids are oily substances. The diazonium chlorides are produced by dissolving the base in glacial acetic acid, passing in a slight excess of hydrogen chloride, and adding amyl nitrite to the cooled solution. The addition of dry ether determines the precipitation of the diazonium chloride as a viscid, colourless oil.

Diazotisation with ethyl nitrite gives a similar result. The least

coloured products are obtained by diazotising with dry reagents in the dark, as the newly prepared compounds are very sensitive to light and moisture. The diazonium sulphates and acetates are also viscid oils. With the object of obtaining solid diazonium salts of these two bases, the diazonium chloride was treated in aqueous solution with the alkali salts of a large selection of inorganic and organic acids. These attempts were unavailing, except in the case of the molybdates, tungstates, phosphomolybdates, and phosphotungstates, when solid, colourless diazonium salts were precipitated.

Benzoylmethyl-p-aminobenzenediazonium molybdate,



was obtained as a white precipitate from benzoylmethyl-*p*-aminobenzenediazonium chloride and sodium molybdate in aqueous solution :

0.1424 gave 0.0722 MoO_3 . Mo = 33.80.

$\text{C}_{14}\text{H}_{15}\text{O}_9\text{N}_3\text{Mo}_2$ requires Mo = 34.22 per cent.

When dried over phosphoric oxide, this substance retained its white colour for an indefinite time. The corresponding diazonium tungstate was similarly prepared, but owing to its greater solubility in water or aqueous sodium tungstate it was not isolated in a state of purity.

Benzoylethyl-p-aminobenzenediazonium molybdate,



was also obtained as a white precipitate :

0.3421 gave 19.2 c.c. N_2 at 25° and 771 mm. N = 6.36.

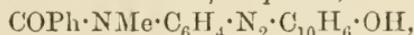
0.1291 „ 0.0651 MoO_3 . Mo = 33.62.

$\text{C}_{15}\text{H}_{17}\text{O}_9\text{N}_3\text{Mo}_2$ requires N = 7.30 ; Mo = 33.39 per cent.

The corresponding tungstate was obtained as a white precipitate, which, owing to its greater solubility, could not be completely freed from sodium tungstate.

The diazonium salts of the two alkylated benzoyl-*p*-phenylenediamines, whether solid or oily, couple readily with alkaline β -naphthol.

Benzoylmethyl-p-aminobenzeneazo- β -naphthol,



is insoluble in water, but dissolves readily in alcohol, from which solvent it separates in dark crimson crystals with a green reflex ; its melting point is 152° :

0.1739 gave 16.5 c.c. N_2 at 20.5° and 750 mm. N = 10.69.

$\text{C}_{23}\text{H}_{19}\text{O}_2\text{N}_3$ requires N = 11.02 per cent.

Benzoylethyl-p-aminobenzeneazo- β -naphthol,



is a scarlet-red compound, crystallising somewhat indefinitely from acetic acid, alcohol, or ethyl acetate, and melting at 174 — 175° :

0.2695 gave 26.4 c.c. N_2 at 20° and 764 mm. $N = 11.27$.

$C_{25}H_{21}O_2N_3$ requires $N = 10.63$ per cent.

These azo-derivatives develop deep purple colorations with concentrated sulphuric acid.

Diazoamines from Benzoyl-p-phenylenediamine and its N-Alkyl Homologues.

Dibenzoyl-4 : 4'-diaminodiazaminobenzene,



—This compound was obtained by the interaction of benzoyl-*p*-phenylenediamine and its diazonium chloride, the former being dissolved in alcohol and the latter in water. A development of colour indicates the production of the diazoamine, and the product is deposited as an orange-brown precipitate on the addition of sodium acetate, which decomposes rapidly in contact with aqueous solutions. When quickly collected and dried it decomposed at 186° :

0.1058 gave 14.6 c.c. N_2 at 20° and 767.6 mm. $N = 15.95$.

$C_{26}H_{21}O_2N_3$ requires $N = 16.09$ per cent.

Although insoluble in water, the diazoamine dissolved readily in alcohol.

Dibenzoyldimethyl-4 : 4'-diaminodiazaminobenzene,



—The oily benzoylmethylaminobenzenediazonium chloride was dissolved in water and added to an alcoholic solution of *as*-benzoylmethyl-*p*-phenylenediamine. The mixture remained clear, and the diazoamine was slowly precipitated by the addition of aqueous sodium acetate. The product was a pale yellow substance, readily soluble in alcohol, and decomposing at 146° :

0.1699 gave 21.7 c.c. N_2 at 19.2° and 764.3 mm. $N = 14.77$.

$C_{28}H_{25}O_2N_5$ requires $N = 15.12$ per cent.

Dibenzoyldiethyl-4 : 4'-diaminodiazaminobenzene,



—This diazoamine resembled the preceding compound, and was produced in a similar manner ; it decomposed at about 104° :

0.2289 gave 27.4 c.c. N_2 at 19.7° and 764.9 mm. $N = 13.80$.

$C_{30}H_{29}O_2N_5$ requires $N = 14.26$ per cent.

These diazoamines were resolved into their generators on treatment with cold concentrated hydrochloric acid, the presence of the diazonium chloride being detected by the interaction with alkaline β -naphthol. The diazoamines themselves do not couple with this reagent.

Interaction of the Foregoing Diazonium Salts with Ammonia and Sodium Hydroxide.

1. *Benzoyl-p-aminobenzenediazonium Chloride.*

(a) *Action of Aqueous Sodium Hydroxide.*—The addition of this alkali to an aqueous solution of the diazonium chloride produces a yellow coloration, and gradually a brown solid separates, this change being accompanied by the evolution of nitrogen. After several hours the generation of gas ceases, and an electrolyte, such as sodium chloride or acetate, is added to coagulate the colloidal precipitate. The product is collected after twelve hours, and is then sufficiently granulated to be washed without dissolving again to a colloidal solution. The dried diazo-oxide is very easily electrified; it decomposes indefinitely at 162°, and dissolves readily in alcohol, but does not crystallise easily:

0.1269 gave 0.3298 CO₂ and 0.0608 H₂O. C = 70.87; H = 5.32.

0.1868 ,, 19.8 c.c. N₂ at 20° and 754 mm. N = 12.03.

C₂₆H₂₀O₃N₄ requires C = 71.57; H = 4.59; N = 12.84 per cent.

(b) *Action of Ammonia.*—The interaction of ammonia and benzoyl-*p*-aminobenzenediazonium chloride in aqueous solution gives rise to a change similar to that observed in the reaction with sodium hydroxide, but in this case the yellowish-brown product is a mixture of diazoamine and diazo-oxide, decomposing at about 135°. The nitrogen estimations were made on different preparations:

0.1462 gave 0.3772 CO₂ and 0.0752 H₂O. C = 70.34; H = 5.71.

0.2041 ,, 24.8 c.c. N₂ at 22° and 766.7 mm. N = 13.89.

0.1038 ,, 13.1 c.c. N₂ ,, 20° ,, 742 mm. N = 14.09.

The diazoamine, C₂₆H₂₁O₂N₅, requires C = 71.73; H = 4.83; N = 16.09 per cent., whilst the diazo-oxide should contain 12.84 per cent. of nitrogen.

These experiments with sodium hydroxide and ammonia were repeated in the volumeter, when it was found that in the former case 1.7 atoms, and in the latter 1.8 atoms, of nitrogen were liberated from two molecular proportions of the diazonium chloride.

2. *Benzoylmethyl-p-aminobenzenediazonium Chloride.*

(a) *With Sodium Hydroxide.*—The alkali determined the gradual separation of an orange-brown solid from the aqueous solution of this diazonium salt, the change being accompanied by the evolution of nitrogen. The product was left to coagulate, and then collected and dried. It was soluble in alcohol, but did not crystallise readily. Analysis showed that the substance was a diazo-oxide:

0.1233 gave 0.3268 CO_2 and 0.0623 H_2O . $\text{C} = 72.30$; $\text{H} = 5.71$.

0.1072 ,, 11.6 c.c. N_2 at 24° and 759 mm. $\text{N} = 12.11$.

$\text{C}_{28}\text{H}_{24}\text{O}_3\text{N}_4$ requires $\text{C} = 72.41$; $\text{H} = 5.17$; $\text{N} = 12.07$ per cent.

The diazo-oxide decomposed indefinitely at 145° .

(b) *With Ammonia*.—The addition of ammonia to the solution of the diazonium chloride leads to the production of a bright orange precipitate, which decomposed at 146° , and was apparently identical with the diazoamine obtained synthetically (p. 1326) :

0.1292 gave 0.3426 CO_2 and 0.0674 H_2O . $\text{C} = 72.31$; $\text{H} = 5.80$.

0.2643 ,, 34.2 c.c. N_2 at 24° and 763 mm. $\text{N} = 14.55$.

$\text{C}_{28}\text{H}_{25}\text{O}_2\text{N}_5$ requires $\text{C} = 72.56$; $\text{H} = 5.40$; $\text{N} = 15.12$ per cent.

3. *Benzoylethyl-p-aminobenzenediazonium Chloride*.

(a) *With Sodium Hydroxide*.—The addition of the alkali to an aqueous solution of the diazonium salt gave rise to the evolution of nitrogen (one molecule from two molecules of salt) and the formation of a brown precipitate, which was soluble in alcohol, ether, or benzene.

This diazo-oxide decomposed at about 90° :

0.1264 gave 0.3425 CO_2 and 0.0672 H_2O . $\text{C} = 73.87$; $\text{H} = 5.91$.

0.2157 ,, 21.5 c.c. N_2 at 21° and 743 mm. $\text{N} = 11.09$.

$\text{C}_{30}\text{H}_{28}\text{O}_3\text{N}_4$ requires $\text{C} = 73.16$; $\text{H} = 5.69$; $\text{N} = 11.39$ per cent.

(b) *With Ammonia*.—In this case the product was probably identical with the diazoamine obtained synthetically (see p. 1326). This preparation, which decomposes at about 99° , was soluble in alcohol, ether, or benzene ; it did not, however, crystallise readily from any of these solvents :

0.1047 gave 0.2792 CO_2 and 0.0584 H_2O . $\text{C} = 72.73$; $\text{H} = 6.20$.

0.1230 ,, 0.3282 CO_2 ,, 0.0683 H_2O . $\text{C} = 72.78$; $\text{H} = 6.17$.

0.5139 ,, 62 c.c. N_2 at 23° and 757.5 mm. $\text{N} = 13.55$.

$\text{C}_{30}\text{H}_{29}\text{O}_2\text{N}_5$ requires $\text{C} = 73.31$; $\text{H} = 5.91$; $\text{N} = 14.26$ per cent.

Although these diazoamines and diazo-oxides were not produced in a definitely crystalline condition, nevertheless satisfactory analytical results were obtained from the thoroughly dried substances, owing to the fact that in every case very carefully purified base was employed in their preparation.

Neither the diazoamines nor diazo-oxides coupled directly with alkaline β -naphthol, but when previously treated with mineral acid (especially hydrochloric acid in glacial acetic acid solution) the presence of a diazonium chloride was indicated by the azo-condensation with the β -naphthol.

In the reactions with sodium hydroxide, the amount of nitrogen liberated was measured in the volumeter, and found to correspond

with one molecular proportion of the gas from two molecules of diazonium salt. The mother liquors were carefully tested for nitrite, but in no case could any be detected. Half the nitrogen originally present in the diazonium salt is liberated as such, the remainder being present in the diazo-oxide.

ROYAL COLLEGE OF SCIENCE, LONDON,
SOUTH KENSINGTON, S. W.

CXLVII.—*isoIminazolone*.

By HENRY JOHN HORSTMAN FENTON and WILLIAM ARTHUR
REGINALD WILKS, B.A.

SEVERAL observations have already been recorded on the condensation of dihydroxymaleic acid with organic bases. In the examples so far studied, the changes take place with elimination of either one or two molecules of carbon dioxide, so that the resulting products may be regarded as if they were derived from either tartronic semi-aldehyde (hydroxypyruvic acid or dihydroxyacrylic acid) or from glycollaldehyde.

Thus, the action of phenylhydrazine yields, in the first place, Nastvogel's osazone, $\text{CH}(\text{:N}_2\text{HPh})\cdot\text{C}(\text{:N}_2\text{HPh})\cdot\text{CO}_2\text{H}$. and afterwards, the dihydrazone of glyoxal, $\text{CH}(\text{:N}_2\text{HPh})\cdot\text{CH}(\text{:N}_2\text{HPh})$. With ammonia, in aqueous solution, the result is pyrazine-2:5-dicarboxylic acid, and the formation of this substance from tartronic semi-aldehyde is easily intelligible (compare *Trans.*, 1905, 87, 808).

When dihydroxymaleic acid is oxidised by mercuric chloride, or by ferric salts, the initial product is mesoxalic semi-aldehyde, and this readily condenses with carbamide, with loss of carbon dioxide, to give glycoluril. There is some probability that in this case the initial product is glycolurilcarboxylic acid, $\text{C}_4\text{H}_5\text{O}_2\text{N}_4\cdot\text{CO}_2\text{H}$, which differs in composition from uric acid by one molecule of water. It appeared to be a matter of interest, therefore, to study the condensation of dihydroxymaleic acid itself with carbamide in the hope of obtaining a purine derivative, possibly, for example, an isomeride of xanthine. It is expected that with certain modifications of detail it may yet be possible to attain this object; the direct experiments so far carried out have, however, yielded a different result, the nature of which is briefly described in the present communication.

When an intimate mixture of anhydrous dihydroxymaleic acid

(1 mol.) and dry carbamide (2 mols.) is heated on a water-bath for about two hours, a rather vigorous reaction takes place in the first instance, carbon dioxide and ammonia being evolved in abundance, with considerable frothing of the mixture. A colourless, transparent liquid eventually results, which sets to a glassy solid on cooling; this dissolves very easily in water, but only to a limited extent in absolute alcohol, and proves to be a mixture of at least two compounds. If this product is repeatedly extracted with boiling alcohol, the alcoholic solution on evaporation leaves a somewhat gummy residue, which, when treated with small quantities of cold water, leaves a mass of transparent crystals. These are very sparingly soluble in cold water, but dissolve easily in hot water, from which the substance separates in large, lustrous, and well-defined pyramids. When heated, they darken at about 225° , and melt completely at 245° .

Dr. A. Hutchinson has very kindly undertaken the examination of these crystals, and the following is his report:

System.—Tetragonal, probably holohedral.

$$c' = 0.7063.$$

Forms present: $a\{100\}$ quite small and not found on all crystals, $p\{111\}$ large. Owing to the predominance of the form p , the crystals are of pyramidal octahedral habit. The crystals are remarkable in that the angle $ap = 100:111$ is 60° . Hence it follows that the angle $pp'' = 111:\bar{1}\bar{1}\bar{1}$ is 90° .

Optically the crystals are uniaxial and negative.

Aqueous solutions of this substance give an intense blood-red colour with ferric chloride; when heated with hydrochloric acid and a drop of hydrogen dioxide, a beautiful pink colour is obtained. The most striking reaction, however, is obtained when a solution of the substance is evaporated to dryness on a water-bath with chlorine water, or with hydrochloric acid and a trace of potassium chlorate. The residue so obtained has a brilliant pink colour, and this, when treated with ammonia, is changed to violet. Sodium hydroxide changes it to a bright rose-red.

This behaviour so closely resembles that of uric acid and of certain other purine derivatives that the authors were, not unnaturally, inclined in the first instance to infer that a compound of this nature had been obtained. It is considered probable that some of the older observers may, in fact, have been dealing with the substance now described when they assumed, from the colour reaction mentioned, the presence of uric acid.

The analytical results clearly demonstrate, however, that the substance is a condensation product of carbamide and a compound containing two atoms of carbon:

I. 0.1237 gave 0.1951 CO₂ and 0.0552 H₂O. C=43.01; H=4.95.
 II. 0.1214 ,, 34.6 c.c. N₂ at 16° and 766 mm. N=33.74.

C₃H₄ON₂ requires C=42.85; H=4.76; N=33.33 per cent.

Molecular-weight determinations by the cryoscopic method, using acetic acid as solvent, gave the following result:

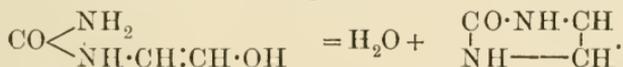
0.1281 in 17.31 acetic acid gave $\Delta t = -0.378$. M.W.=75.

0.1931 ,, 17.31 ,, ,, $\Delta t = -0.569$. M.W.=76.

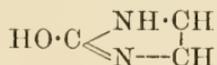
C₃H₄ON₂ requires M.W.=84.

The known substances which have this molecular formula are the following: Ruhemann's pyrazolone (m. p. 156°), Rothenberg's pyrazolone (oil), cyanoacetamide (m. p. 120°), methylparacyanofornamide (m. p. 260°), acetylcyanamide (syrup), Angeli's keto-diazopropane (oil), Letsche's hydroxypyrazole, Abel's compound from epinephrin (not isolated), and lastly, Marckwald's μ -iminazolone (*Ber.*, 1892, **25**, 2357). With the exception of the last-named compound all these substances are obviously excluded by their properties or mode of formation. (The colour reaction with ferric chloride did, indeed, suggest the possibility that the substance might be pyrazolone, but comparison with a specimen kindly supplied by Dr. Ruhemann showed that there is no real resemblance.)

Marckwald (with Ellinger) obtained μ -iminazolone by heating the hydrochloride of aminoacetal in concentrated aqueous solution with slight excess of potassium cyanate; a crystalline product melting at 105° is thus obtained, which proves to be acetylcyanamide, NH₂·CO·NH·CH₂·CH(OEt)₂; this, when dissolved in water and heated with a few drops of sulphuric acid, yields the iminazolone. The change is represented in the following way, the acetal of hydantoic aldehyde being an intermediate stage:



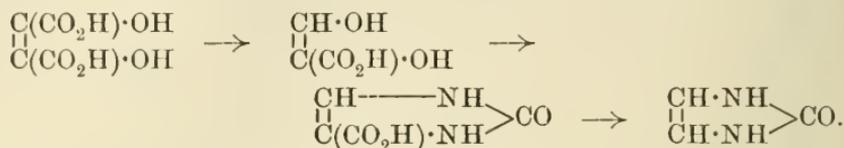
The possibility of the tautomeric formula



is also suggested. This product is described as indistinctly crystalline, easily soluble in hot water, and as possessing weakly acidic and basic properties; it decomposes above the boiling point of concentrated sulphuric acid. No mention is made of any colour reactions.

The mode of formation of the compound now obtained by the present authors would at once suggest that it has the constitution which Marckwald assigns to his μ -iminazolone. It might be supposed, for example, that the initial stage consists in the

formation of glycollaldehyde, and that this then condenses with carbamide. Or, that dihydroxyacrylic acid is first produced, which by condensation with carbamide gives iminazolonecarboxylic acid, and that the latter subsequently loses carbon dioxide:



The latter view appears to be more probable, since experiments made with pure glycollaldehyde and carbamide have so far failed to give the product in question under conditions similar to those employed in its formation from dihydroxymaleic acid.

It appeared desirable, therefore, to make a close comparison between this product and Marckwald's compound, especially as the properties seemed to differ notably in certain respects. The authors have been enabled to make this comparison owing to the kindness of Professor Marckwald, who has supplied them with a small specimen of μ -iminazolone. As a result, it is found that the two compounds are markedly different; repeated purification fails to show any distinct crystalline form of μ -iminazolone, and no acetyl compound could be obtained from it by the treatment mentioned below. It does, however, show faint indication of the colour reactions referred to, and, since Professor Marckwald does not guarantee that the specimen he sends is the same as the product analysed, the question as to identity cannot be conclusively settled. Owing to the very considerable difference in properties observed, the present authors consider that for their product the title *isoiminazolone* is perhaps the most appropriate.

Acetyl Derivative.—When the substance just described is heated for a few minutes with excess of acetic anhydride, and the excess of the reagent is then removed by distillation, a residue is left which, on cooling, sets to a crystalline mass. This, when recrystallised from ether, is obtained in silky needles which melt at 106° :

0.1471 gave 0.2593 CO_2 and 0.0662 H_2O . C=48.07; H=5.00.

$\text{C}_3\text{H}_3\text{ON}_2(\text{CH}_3\cdot\text{CO})$ requires C=47.62; H=4.76 per cent.

In addition to *isoiminazolone*, the condensation of dihydroxymaleic acid with carbamide may give rise to at least three other products:

(a) The mixture obtained by heating the substances together in the proportion of two molecules of carbamide to one of the acid is extracted with alcohol in the manner described above in order to obtain the *isoiminazolone*. The residue is extremely easily

soluble in cold water, and if the aqueous solution is poured into an excess of alcohol, a very voluminous, white precipitate is obtained, which appears, under the microscope, to be indistinctly crystalline. After repeated purification by solution in water and precipitation with alcohol, this product gives no colour with ferric chloride, but if kept for some days it gives a colour corresponding with that produced by *isoiminazolone*, although it is much less intense. When boiled with barium hydroxide, a bulky, brown precipitate separates, and the filtrate, after neutralisation, now gives a fairly intense blood-red colour with ferric chloride. Analysis of this product, dried in a vacuum desiccator, gave C=35.1, H=5.59, N=26.8 per cent. Other specimens, however, prepared in a similar way, gave somewhat different numbers, and it is therefore rather doubtful whether the product is a definite substance. The numbers mentioned correspond fairly well with the formula $C_3H_6O_2N_2$, which requires C=35.3, H=5.88, N=27.4 per cent.; it is therefore not improbable that the product consists essentially of hydantoic aldehyde, $NH_2 \cdot CO \cdot NH \cdot CH_2 \cdot CHO$, but that, owing to the instability of this compound, the products analysed had a somewhat variable composition.

(b) When dihydroxymaleic acid and carbamide are heated together in equal molecular proportions, a certain amount of *isoiminazolone* is produced, and may be extracted as before from the mixture. But in this case the principal product is a substance which dissolves very easily in hot water, and immediately separates on cooling as a milky, colloidal suspension. The mixture remains in this condition even after keeping for twenty-four hours or longer, but coagulation almost immediately takes place on the addition of a minute quantity of an electrolyte, such as ammonium chloride. The solid so obtained appears to be amorphous, and is practically insoluble in cold water; its solutions give no colour with ferric chloride.

(c) When dihydroxymaleic acid and carbamide are heated in aqueous solution with a few drops of concentrated hydrochloric acid, a dark brown powder separates, which dissolves in concentrated hydrochloric acid, giving a red solution. This colour is intensified if an oxidising agent, such as hydrogen dioxide, is added, whereas reduction with zinc and dilute acid destroys the colour. Addition of hydrogen dioxide to the reduced solution immediately restores the colour, and the operations may be repeated almost indefinitely without material diminution of the colour intensity. The same brown substance is obtained if glycollaldehyde is condensed with carbamide in a similar way, and the colour effects mentioned may serve as a fairly delicate test for the

identification of glycollaldehyde or of substances which give rise to it on decomposition.

It is the intention of the authors to make a further investigation of the various products here mentioned when sufficient material can be prepared.

The principal part of the expense incurred in carrying out this investigation has been defrayed by means of a grant kindly supplied by the Government Grant Committee of the Royal Society.

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

CXLVIII.—*Homologues of Furfuraldehyde.*

By HENRY JOHN HORSTMAN FENTON and FRED ROBINSON, B.A., B.Sc.

It has been shown in previous communications (Fenton and Gostling, *Trans.*, 1899, **75**, 423; 1901, **79**, 807) that the chloro- and bromo-derivatives of methylfurfuraldehyde are readily obtained by the action of the corresponding halogen acids on keto-hexoses or on cellulose. The yield from these carbohydrates is about 20 per cent. of the theoretical amount, whereas the aldo-hexoses give rise to mere traces only. The halogen atom in these compounds is extremely reactive, the interaction with silver nitrate, for example, being quantitative and practically instantaneous; when boiled with water in presence of barium carbonate, they are completely hydrolysed, yielding the hydroxy-derivative. Finely divided metallic silver readily removes the halogen from the bromo-derivative, the residual groups uniting to form difurylethanedialdehyde. Treatment with sulphurous acid converts the halogen compounds into a substance having the molecular formula $C_{11}H_8O_4$, to which the constitution of methylfuryl is provisionally assigned. This compound shows remarkable colour reactions with primary amines, with carbamides, and with strong bases, and various applications of these reactions have already been suggested (*Proc. Camb. Phil. Soc.*, 1906, **13**, 298). The action of malonic ester on the halogen derivatives in presence of alcoholic potash gives rise to a compound, still under investigation, which has strongly marked fluorescent properties; the formation of this compound affords a very delicate test for the mono- and poly-hexoses, and serves to distinguish them from the pentoses, etc. (*loc. cit.*, 1907, **14**, 24).

Investigation of the properties and relations of the various compounds here mentioned is now being continued, and in the present communication a brief account is given of some of the results which have recently been obtained.

Application of the Friedel and Crafts Reaction.

A mixture of chloromethylfurfuraldehyde (10 grams), anhydrous aluminium chloride (7 grams), and excess (25 c.c.) of benzene was heated in a reflux apparatus for about two hours. Reaction began at about 40° with copious evolution of hydrogen chloride, and the temperature was regulated so as to keep the liquid in a state of gentle ebullition. The resulting dark, nearly opaque mixture was then allowed to cool, poured on to powdered ice, and submitted to steam distillation. The first portions of the distillate contained some of the product of the reaction dissolved in excess of benzene; afterwards the main portion of the product passed over as an oil, which, on keeping, solidified to a crystalline mass. After recrystallisation several times from a mixture of ether and light petroleum, the product was obtained in large, colourless prisms, melting without decomposition at 30·5—31°. The total yield was about 6 grams:

0·1229 gave 0·3452 CO₂ and 0·0602 H₂O. C = 76·65; H = 5·44.

0·1917 ,, 0·5403 CO₂ ,, 0·0926 H₂O. C = 76·86; H = 5·37.

C₁₂H₁₀O₂ requires C = 77·41; H = 5·37 per cent.

The molecular weight was determined by the cryoscopic method, using acetic acid and benzene as solvents:

With benzene the results were as follows:

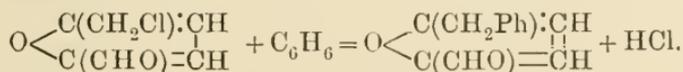
0·2946, in 16·34 benzene, gave $\Delta t = -0·495$. M.W. = 182.

0·5043 ,, 16·34 ,, ,, $\Delta t = -0·875$. M.W. = 176.

0·1390 ,, 15·18 acetic acid, gave $\Delta t = -0·205$. M.W. = 174.

C₁₂H₁₀O₂ requires M.W. = 186.

The mode of formation and molecular formula of this compound clearly indicate that it is benzylfurfuraldehyde, the change being represented thus:



Benzylfurfuraldehyde has a faint aromatic odour, somewhat resembling that of nitrobenzene; it is almost insoluble in cold water, but dissolves readily in alcohol, benzene, ether, petroleum, or acetic acid.

The aldehydic character is evidenced by the usual reactions; it yields a silver mirror on warming with ammoniacal silver nitrate, and reduces Fehling's solution only, however, on heating. Its solution in acetic acid yields with phenylhydrazine a milky precipitate, which

settles only to an oil; if, however, the alcoholic solution is mixed with phenylhydrazine in slight excess and left in a vacuum desiccator, a crystalline mass is obtained, which, when washed with ether and recrystallised from a mixture of alcohol and toluene, melts at 199—204°.

The *phenylbenzylhydrazide* is more easily obtained; acetic acid solutions of phenylbenzylhydrazine and benzylfurfuraldehyde when warmed together yield, after a time, a white or yellow precipitate, which, after washing with acetic acid and ether and recrystallising from benzene and light petroleum, melts at 133° :

0.2440 gave 16.6 c.c. N_2 at 15° and 760 mm. $N = 8.09$.

$C_{25}H_{22}ON_2$ requires $N = 7.66$ per cent.

The *oximes* of benzylfurfuraldehyde are obtained in a manner analogous to that employed by Goldschmidt and Zanoli (*Ber.*, 1892, 25, 2573) in the preparation of the oximes of furfuraldehyde.

A solution of 3.14 grams of sodium hydroxide in 20 c.c. of water was mixed with 1.1 grams of hydroxylamine hydrochloride in 5 c.c. of water, and to the well-cooled mixture, 2 grams of benzylfurfuraldehyde, dissolved in a little ether, were gradually added. The resulting mixture was continuously shaken, and a stream of carbon dioxide was passed into it, during which process the liquid becomes yellow. After extraction with ether and evaporation of the ethereal solution, the product separates in pale yellow needles or prisms, which melt at 96—97°; these when repeatedly crystallised from light petroleum become colourless and then melt at 99°. This product is practically insoluble in water, but dissolves easily in organic solvents :

0.2695 gave 15.7 c.c. N_2 at 12° and 757 mm. $N = 6.95$.

$C_{12}H_{11}O_2N$ requires $N = 6.99$ per cent.

By this method of treatment Goldschmidt and Zanoli (*loc. cit.*) obtained the *anti*-aldoxime of furfuraldehyde; Fromherz and Meigen, proceeding in the same way with methylfurfuraldehyde, obtained a product which was at first considered to be a mixture, but which on further investigation was shown in all probability to be the *anti*-aldoxime. In order to prepare methylfurfuraldehyde *syn*-oxime, the authors named treated the *anti*-compound in ethereal solution with hydrogen chloride, and decomposed the resulting salt with sodium hydroxide. The benzylfurfuraldehyde compound obtained in the manner described above was therefore subjected to a similar treatment; on passing the gas into the colourless solution, crystals separated, and the liquid became pale yellow. The ethereal solution on evaporation deposited a mass of crystals; these were washed with a little ether and with water, mixed with excess of aqueous sodium hydroxide, and warmed for five minutes on a water-bath. The rather

yellow liquid so obtained, on cooling, deposited lustrous, silver-white prisms, which melted at $121-122^{\circ}$ and, after recrystallisation from light petroleum, at 124° :

0.2245 gave 13.7 c.c. N_2 at 22° and 755 mm. $N = 7.04$.

$C_{12}H_{11}O_2N$ requires $N = 6.99$ per cent.

From analogy to the methylfurfuraldehyde compounds, there appears to be little doubt therefore that the two compounds here described are the *anti*- and *syn*-oximes respectively of benzylfurfuraldehyde. Both compounds when dissolved in dry ether, mixed with slight excess of phenylcarbimide, and kept for twenty-four hours, yield crystalline products; the properties of the derivatives appear also to be different, but they have not yet been thoroughly studied.

The properties of benzylfurfuraldehyde are in many other respects analogous to those of methylfurfuraldehyde; thus, when concentrated sulphuric acid is carefully added to a dilute solution of benzylfurfuraldehyde in alcohol, a bright blue colour is developed (Maquenne's reaction for methylfurfuraldehyde gives a green colour). Phloroglucinol in presence of concentrated hydrochloric acid gives an orange-red colour; resorcinol produces a somewhat similar effect, and with pyrogallol the colour is crimson; when warmed with carbamide and hydrochloric acid a violet colour results. Aniline acetate gives a yellow colour changing to red.

The oxidation of benzylfurfuraldehyde to benzylpyromucic acid has been attempted in various ways; the method of oxidation by silver oxide in presence of sodium carbonate, which was employed by Hill in the preparation of methylpyromucic acid from methylfurfuraldehyde, yields a colourless, crystalline acid, which has a penetrating frankincense-like odour. The same product is obtained by oxidation of the aldehyde with alkaline potassium permanganate at 20° , according to the method used by Volhard in the preparation of pyromucic acid (*Annalen*, 1891, 261, 379); also, by heating the aldehyde with alcoholic potassium hydroxide, evaporation, extraction with ether, and acidification of the aqueous solution which remains. In all cases, however, the yield is extremely poor and the purification difficult. The partly purified acid melted at $167-169^{\circ}$. The authors intend to make a further study of this acid, when a further supply of material is available, with the object of obtaining benzylfuran.

It is evident that this synthetical method of preparing substituted furfuraldehydes may, if desired, be greatly extended, and the authors propose to make further experiments in this direction.

When toluene and chloromethylfurfuraldehyde interact in presence of aluminium chloride, a product is obtained, on steam distillation, which solidifies to a white solid melting at 74.5° . It is nearly insoluble

especially since the two modes of formation of the hydroxy-aldehyde are so closely allied.

The present authors have now obtained a result which affords a fairly conclusive proof of the correctness of the formula previously assigned to chloro- and bromo-methylfurfuraldehyde, and consequently to the hydroxy-compound which these compounds yield on hydrolysis. When the chloro-derivative is warmed with excess of nitric acid (D about 1.3), a violent action ensues, and the resulting liquid, on evaporation, yields a white, crystalline mass. This product, which is free from chlorine, is very sparingly soluble in cold water, but dissolves easily in boiling water; it crystallises from the latter in needles or prisms, which partly sublime when heated, and show no signs of melting at the boiling point of concentrated sulphuric acid:

0.1005 gave 0.1697 CO_2 and 0.0258 H_2O . C = 46.05; H = 2.85.

$\text{C}_6\text{H}_4\text{O}_5$ requires C = 46.15; H = 2.57 per cent.

The properties of this product agree entirely with those of furan-2:5-dicarboxylic acid (dehydromucic acid); ferric chloride, for example, gives the well-known characteristic reaction; an aqueous solution of the acid is mixed with a few drops of the reagent and warmed, when a transparent jelly separates.

This result then clearly indicates that the halogen must have occupied the ω -position, and is altogether irreconcilable with the formula suggested for Dull's compound.

The authors consider that, on the whole, the balance of evidence strongly favours the view that the two hydroxymethylfurfuraldehydes mentioned are identical, and that the position commonly assigned to the hydroxyl group in Dull's compound is incorrect.

Preparation of Chloromethylfurfuraldehyde.

Many attempts have been made to improve on the methods previously given for the preparation of the halogen derivatives of methylfurfuraldehyde. Although the yield obtained by these methods is good, the process of extraction is very troublesome when lævulose or sucrose is used, owing to the presence of tarry "humus" substances, and also to the large excess of acid which is necessarily present. The preparation from cellulose avoids these difficulties to some extent, but in this case the operation has to be performed under pressure, and is attended with some danger. Although no substantial improvement has been effected in the preparation of the products on a fairly large scale, the following simple process is found to be very rapid and convenient when only small quantities are required, since it permits the use of aqueous acids.

Lævulose is mixed with about twice its weight of solid calcium

chloride, and the mixture is made into a thin paste by stirring it with concentrated aqueous hydrochloric acid. It is then warmed for a few minutes on a water-bath with constant stirring, until the whole mass is dark brown or nearly black, and is suddenly cooled before actual charring takes place. The excess of acid is then removed by careful addition of solid sodium carbonate, and the mixture is extracted with chloroform. On distilling off the chloroform, the chloromethylfurfuraldehyde remains as a syrup, which, when well cooled and rubbed with a rod, often sets to a crystalline mass. In most cases, however, it is best to purify the product by recrystallisation from hot petroleum, and to promote crystallisation by contact with a trace of the compound which has been previously prepared.

The bromo-compound can be prepared in a similar way, using calcium bromide, or even potassium bromide, and concentrated aqueous hydrogen bromide.

An attempt to obtain the fluoro-compound in this way, using potassium hydrogen fluoride and hydrofluoric acid, has not so far been successful. If calcium chloride and hydrofluoric acid are used, the chloro-compound only results.

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

CXLIX.—*Studies of Dynamic Isomerism. Part IX.*
The Relationship between Absorption Spectra and
Isomeric Change. Absorption Spectra of Sulphonic
Derivatives of Camphor.

By THOMAS MARTIN LOWRY and CECIL HENRY DESCH.

In a recent paper on the "Absorption Spectra of the Halogen, Nitro- and Methyl Derivatives of Camphor" (this vol., p. 807) it was shown that the isomeric changes which several of these substances undergo are not directly associated with the presence or absence of bands in their absorption spectra. Thus, to quote the two most striking cases, nitrocamphor, which changes readily in neutral and in alkaline solutions, produces an absorption band only under the latter conditions, but α -bromocamphor, which undergoes isomeric change only in presence of alkalis, gives a strong absorption band in acid, neutral, and alkaline solutions indifferently.

The investigation of the isomeric changes of the sulphonic derivatives (Trans, 1906, 89, 1042) had presented several points of interest—

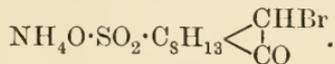
especially in reference to the interaction of the carbonyl group of the camphor molecule with the sulphonic group of the Reychler or β -series of compounds—and it was thought desirable to study their absorption spectra in order to corroborate and extend the conclusions arrived at from the study of the simpler compounds described in the previous paper. Observations were therefore made with representatives both of the π - and of the β -series of sulphonic compounds.

In accordance with the scheme described in the earlier paper, the absorption spectra were photographed in such a way that each exposure represented a change of thickness in the ratio 1.26 to 1, an alteration in the ratio 10 to 1 being thus accomplished by means of ten equal geometric intervals. This interval, $\sqrt[10]{10}$ or antilog. 0.1, forms a very convenient unit for measuring the persistence of a band, and is made use of throughout the present paper.

π -Sulphonic Derivatives of Camphor.

Three members of the series were examined (Fig. 1):

(a) *Ammonium α -Bromocamphor- π -sulphonate,*



—This compound is capable of existing in stereoisomeric α - and α' -forms, but does not undergo isomeric change when alkali is added (Trans., 1906, 89, 1043), probably because the potash merely displaces ammonia from the salt, and this base is not sufficiently strong to cause enolisation in the $\cdot\text{CHBr}\cdot\text{CO}\cdot$ complex. In spite of its resistance to isomeric change, extending to alkaline as well as to neutral solutions, the salt shows a strong band persisting over five exposures in $N/100$ -solution, as compared with four exposures for the parent substance, α -bromocamphor.

(b) *α -Bromocamphor- π -sulphonamide,* $\text{NH}_2\cdot\text{SO}_2\cdot\text{C}_8\text{H}_{13}\begin{matrix} \text{CHBr} \\ | \\ \text{CO} \end{matrix}$, is, like

the preceding compound, stable in neutral solutions, but differs from it in that it undergoes isomeric change to the extent of 15 per cent. when a trace of sodium ethoxide is added to the alcoholic solution (*loc. cit.*, p. 1044). The addition of alkali is not necessary, however, for the development of an absorption band, which appears with a persistence of four exposures in the neutral alcoholic solutions.

(c) The *acetyl* derivative, $\text{CH}_3\cdot\text{CO}\cdot\text{NH}\cdot\text{SO}_2\cdot\text{C}_8\text{H}_{13}\begin{matrix} \text{CHBr} \\ | \\ \text{CO} \end{matrix}$, or perhaps $\text{NH}_2\cdot\text{SO}_2\cdot\text{C}_8\text{H}_{13}\begin{matrix} \text{CBr} \\ | \\ \text{C}\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_3 \end{matrix}$, of the preceding compound does not undergo isomeric change either alone or on the addition of a trace of alkali; its alcoholic solution shows, however, an absorption band per-

sisting over five exposures. As its spectrum is almost identical with that of the amide, it is probable that it is correctly represented by the former rather than by the latter formula, and that its failure to undergo isomeric change on the addition of a trace of sodium ethoxide is due to the elimination of the alkali in the form of sodium acetate, rather than to the removal of the mobile hydrogen atom by fixing in the enolic form as shown in the second formula.

β-Sulphonic Acids and their Salts.

The potassium salts, $\text{KO}\cdot\text{SO}_2\cdot\text{C}_8\text{H}_{13}$ $\left\langle \begin{array}{l} \text{CHBr}(\text{Cl}) \\ | \\ \text{CO} \end{array} \right.$, of *α*-bromocamphor- and *α*-chlorocamphor-*β*-sulphonic acids are stable in neutral solutions, but undergo stereoisomeric change on the addition of alkali (Trans., 1906, 89, 1045). The absorption spectra show well marked bands, but these are actually weakened and not strengthened by the addition of an excess of alkali. Thus the chlorocamphor band at $1/\lambda$ 3400, which has a persistence of four exposures in the parent substance, is intensified to a persistence of nine exposures by the introduction of the $\cdot\text{SO}_2\cdot\text{OK}$ group, but falls back to seven exposures when two additional equivalents of alkali are added to the *N*/100-aqueous solution (Fig. 2).

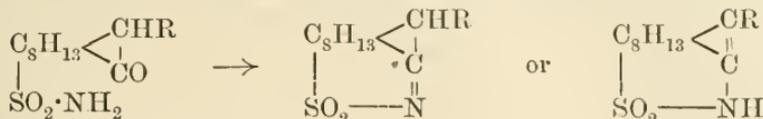
Camphor-*β*-sulphonic acid, $\text{HO}\cdot\text{SO}_2\cdot\text{C}_8\text{H}_{13}$ $\left\langle \begin{array}{l} \text{CH}_2 \\ | \\ \text{CO} \end{array} \right.$, although unable, in the absence of an *α*-substituent, to undergo stereoisomeric change, behaves otherwise in the same way as the *α*-chloro-compound. As in the preceding case, the introduction of the sulphonic group causes an intensification of the band from a persistence of three exposures in camphor to six exposures in the *β*-sulphonic acid and its sodium salt, but the addition of two further equivalents of alkali reduces the persistence again to four exposures only.

A similar repression of the band from eight to six units of persistence by the addition of two equivalents of alkali was noticed in the case of *N*/100-aqueous solutions of ammonium *α*-chloro-*π*-sulphonate, and the phenomenon appears therefore to be a general one in this group of compounds.

β-Sulphonamides and Anhydramides.

The amides and anhydramides are the most interesting of the *β*-sulphonic compounds, owing to the evidence which they afford of the special contiguity of the *β*-position to the *κ*-position occupied by the $\cdot\text{CO}\cdot$ group in camphor. The conversion of the amides into anhydramides by the elimination of a molecule of water is not readily effected by dehydrating agents, but is quickly brought about by acids (Trans., 1902, 81, 1448), or in the case of the parent

sulphonamide by minute traces of sodium ethoxide (Trans., 1906, 89, 1046). In the case of the α -bromo- and α -chloro-sulphonamides the



addition of alkali brings about a partial conversion into the stereoisomeric α' -compounds, and a similar change of smaller magnitude is effected in the anhydramides, probably as in other instances, through the intervention of an "enolic" (sulpholactam) isomeride as formulated above. In contrast to the mono-halogen derivatives, the anhydramides of the $\alpha\alpha'$ -dichloro- and dibromo-sulphonic acids can

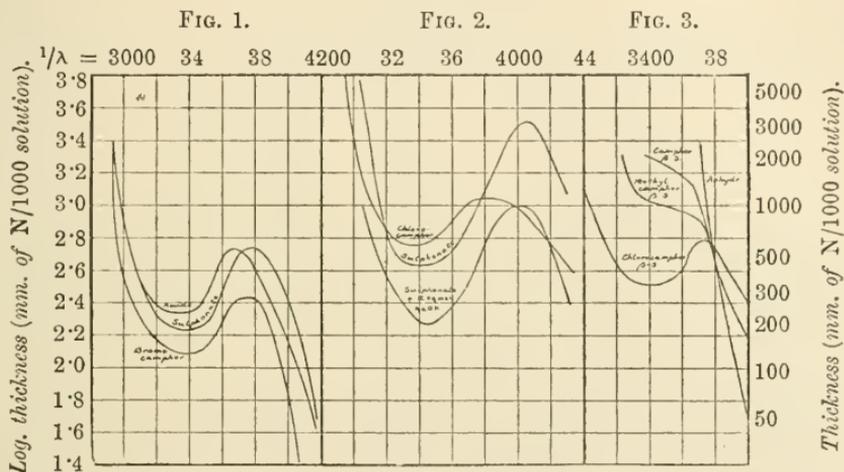


FIG. 1.— α -Bromocamphor, ammonium α -bromocamphor- π -sulphonate, and α -bromocamphor- π -sulphonamide; N/100 solutions in alcohol.

FIG. 2.— α -Chlorocamphor and potassium α -chlorocamphor- β -sulphonate in neutral solution and with 2 equivalents of sodium hydroxide; N/100 solutions in water.

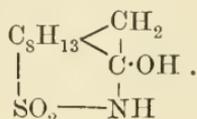
FIG. 3.—Camphor- β -anhydramide and the β -sulphonamides of camphor, α -methylcamphor, and α -chlorocamphor; N/100 solutions in alcohol.

only exist in one form, and do not undergo isomeric change whether alone or in presence of alkali.

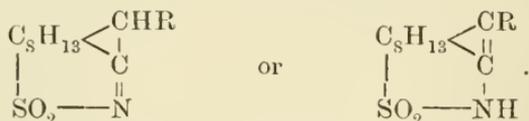
The spectra of this series of compounds proved to be of special interest owing to the steady disappearance of the power to produce absorption bands on passing from bromo- to chloro- and to methyl derivatives, and finally to derivatives of camphor itself (Fig. 3). This is well brought out in the following table.

	Camphor.	Methyl-camphor.	Chloro-camphor.	Bromo-camphor.
Salts	Band	Band	Band	Band
Amides	No band	No band	"	"
Anhydramides.	"	"	No band	"
Disubstituted anhydramides	—	—	"	No band

From this table it appears that the absorption band which is developed by all the salts and by the sulphonamides of α -chloro- and α -bromo-camphor can be eliminated quite as effectively by displacing the halogen atom of the sulphonamides by methyl or by hydrogen, as by the more usual process of displacing the remaining hydrogen by a second halogen atom. In the case of the amides the disappearance of the absorption band might be attributed to an internal condensation of the sulphonamide, which would give rise to a completely saturated molecule:



This explanation cannot, however, be given in the case of the anhydramides, which must all be formulated as:



Of the six anhydramides examined, the dichloro- and dibromo-compounds on the one hand and the camphoranhydramide on the other show no band; of the mono-substituted anhydramides the α -bromo-compound gives a band, but the α -chloro- and α -methyl compounds give rise only to general absorption.

These observations appear to indicate that the development of a band is influenced to a very large extent by substitution, but in a way that bears no direct relationship to the occurrence or even to the theoretical possibility of isomeric change.

Anilides of β -Sulphonic Acids.

The anilides of this series possess the curious property of dissolving in alkalis, possibly owing to the formation of a ring compound, for example:



The absorption curves for the alkaline solutions are characterised by the presence of a band in the far ultra-violet at $1/\lambda$ 4000. This band, which was observed in the case of camphor- β -sulphonanilide, camphor- β -sulpho- p -bromoanilide, α -bromocamphor- β -sulphonanilide, and α -bromocamphor- β -sulpho- p -bromoanilide, is of great intensity, persisting to a thickness of a few millimetres only of $N/10,000$ solution, but does not appear in the neutral solutions, which are one hundred

that is, at a concentration 100 times greater than that at which a band appears in presence of alkalis; we are at present unable to offer any opinion as to its significance.

Piperidides of β -Sulphonic Acids.

Camphor- β -sulphonic acid is characterised by the formation of two isomeric piperidides melting at 56° and at 140° , which have been formulated as :



The α -bromo-compound also exists in two distinct forms melting at 75° and 123° , each of which exhibits a change of solubility on the addition of alkali, and must therefore be capable of undergoing reversible isomeric change (Trans., 1906, 89, 1051). These isomeric compounds are not easy to prepare,* and up to the present we have examined only the absorption spectra of the camphorsulphopiperidide (piperidolactone) melting at 140° and the bromocamphorsulphopiperidide melting at 75° . The former compound shows no selective absorption, but the latter compound gives the bromocamphor band at $1/\lambda$ 3350 with a persistence of four exposures. These observations are in accord with the formulæ that have been assigned to the two compounds, but in view of the somewhat slender evidence on which these formulæ are based, we do not feel justified in drawing any theoretical deductions from the presence or absence of bands in the spectra.

We are indebted to the Research Fund of the Chemical Society for a grant which defrayed a portion of the cost of this investigation, and desire to take this opportunity of expressing our thanks.

130, HORSEFERRY ROAD,
WESTMINSTER.

THE UNIVERSITY,
GLASGOW.

* The camphorsulphopiperidide of lower melting point can be obtained in a crystalline form by slow evaporation of the solvent, but as it liquefies again on the addition of alcohol or petroleum, it is very difficult to purify. Attempts to prepare further quantities of the bromopiperidides have given rise to a new product melting at 86° , the nature of which is under investigation.

CL.—*Studies of the Carbonates. Part I. The Equilibrium between Calcium Carbonate and Carbonic Acid.*

By CLARENCE ARTHUR SEYLER and PERCY VIVIAN LLOYD.

THE object of this investigation was to study the equilibrium between calcium carbonate and carbonic acid under conditions applicable to geological problems. Schlössing's results have been examined by Bodländer (*Zeitsch. physikal. Chem.*, 1900, 35, 32), who has shown how the law observed by Schlössing may be deduced from first principles. Natural waters, however, contain salts which modify the equilibrium, and we have therefore studied their effect.

Method of Experiment.

The solid carbonate, reduced to a coarse powder, was kept with occasional shaking in contact with the solution of carbonic acid and the various salts contained in stoppered bottles completely filled. The temperature was that of the laboratory. Several weeks were required for the attainment of equilibrium. The dissolved carbonate was then titrated with *N*/20-acid, using methyl-orange as indicator, and the free carbonic acid determined by titration with *N*/20-sodium carbonate and phenolphthalein as indicator, using the precautions described by Seyler (*Analyst*, 1897, 22, 312). This method is rapid, and has been shown by Ellms and Bencker (*J. Amer. Chem. Soc.*, 1901, 23, 405) to be more accurate than the original Pettenkofer method or Trillich's modification of it, and to be trustworthy to about 0.02×10^{-3} gram-molecule per litre. This mode of experiment has the advantage over Schlössing's, in which a current of carbon dioxide of known partial pressure is used, since the carbonic acid is directly determined, and the temperature does not require to be kept more than approximately constant.

Equations Governing Equilibrium in Absence of Salts.

We use Bodländer's symbols as follows :

HCO_3 , Ca , etc., in equilibrium equations stand for the concentration of the respective substances in gram-molecules or ions per litre.

k_2 is the dissociation constant of carbonic acid according to the scheme $\text{H}_2\text{CO}_3 = \text{H} + \text{CO}_3$.

k_3 is the dissociation constant of bicarbonates according to the scheme $\text{HCO}_3 = \text{H} + \text{CO}_3$.

k_1 is the "solubility product" of calcium carbonate, namely,
 $k_1 = \text{Ca} \cdot \text{CO}_3$.

k_w is the dissociation constant of water.

The ratio $\frac{k_2}{k_3}$ is the dissociation constant of bicarbonates into carbonates and free carbonic acid according to the scheme $2\text{HCO}_3 = \text{CO}_3 + \text{H}_2\text{CO}_3$.

The condition of equilibrium for this is :

$$\frac{\text{HCO}_3^2}{\text{H}_2\text{CO}_3 \cdot \text{CO}_3} = \frac{k_2}{k_3} \quad \dots \quad (a).$$

Since $\text{Ca} \cdot \text{CO}_3 = k_1$, we have :

$$\frac{\text{HCO}_3^2 \cdot \text{Ca}}{\text{H}_2\text{CO}_3} = \frac{k_2}{k_3} k_1 \quad \dots \quad (b).$$

This is the fundamental equation. If no other lime salts or bicarbonates be present except those due to the dissolved limestone, practically the whole of the calcium will exist in solution as bicarbonate, since CO_3 is always very small. The concentration of the calcium ions (Ca) will always be half that of the bicarbonions (HCO_3), since there are two of the latter for each one of calcium.

Hence we have the concentrations $\text{Ca} = \frac{\text{HCO}_3}{2}$.

Therefore substituting in equation (b) we have :

$$\frac{\text{HCO}_3^3}{\text{H}_2\text{CO}_3} = 2 \frac{k_2}{k_3} k_1 \quad \dots \quad (c).$$

This is Schlössing's law as deduced by Bodländer. The values of the constants $\frac{k_2}{k_3}$ and k_1 are open to discussion, and for the present we shall put $2 \frac{k_2}{k_3} k_1 = F \times 10^{-6}$, where F should be constant. We call it the "saturation factor," since it is a criterion as to whether a water is saturated with limestone or not. We have calculated its value from Schlössing's experiments in which the temperature was 16° , corresponding with a molecular solubility of carbonic acid of 43.5×10^{-3} gram-molecules per litre. It decreases from about 137 for $N/50$ - to about 107 for $N/600$ -solutions (with respect to calcium), the mean being 124.

Experiments were first made on marble and pure limestone with solutions of carbonic acid in order to test our method of working, and the results are given in table I.

TABLE I.

Solid.	Time (days).	$\text{H}_2\text{CO}_3 \times 10^3$.	$2\text{Ca} \times 10^3$.	Ionisation.	$\text{HCO}_3 \times 10^3$.	<i>F</i> .
Marble	43	2.687	7.41	0.88	6.52	103.1
„	75	3.62	8.29	0.88	7.29	107.0
Limestone	44	10.00	12.08	0.87	10.51	116.1
Marble	29	11.40	13.14	0.86	11.30	126.5

The average value of *F* is 113, and the results show a decrease in dilute solutions, as in Schlössing's experiments.

Effect of Other Calcium Salts.

The general equation (b) should hold good, Ca being the total concentration of the calcium ions. We shall have :

$$\frac{\text{HCO}_3^2 \cdot 2\text{Ca}}{\text{H}_2\text{CO}_3} = F \times 10^{-6}.$$

The presence of other calcium salts will therefore diminish the solvent action of water containing carbonic acid upon limestone.

Calcium Chloride.—The solution of this salt was *N*/80, that is, it contained 12.5×10^{-3} gram-equivalents per litre. The degree of dissociation of calcium bicarbonate is assumed to be the same as that of calcium chloride.

TABLE II.

Time.	$\text{H}_2\text{CO}_3 \times 10^3$.	Calcium as bicarbonate $\times 10^3$.	Ionisation.	$\text{HCO}_3 \times 10^3$.	Calcium as chloride.	Ionisation.	Ions.	Total calcium, 2Ca .	<i>F</i> .
12	3.95	6.13	0.845	5.18	12.5	0.845	10.56	15.74	107

Calcium Sulphate.—The concentration of this salt was from 2.382×10^{-3} , corresponding with about 8.4 degrees of permanent hardness on Clark's scale, to 12.5×10^{-3} , or 44 degrees of hardness. The degree of dissociation was calculated approximately by dividing the water between the bicarbonate and sulphate in such proportions as to give isohydric solutions, and finding the degree of dissociation which each would have if dissolved in its respective volume of water.*

* An example will make clear the method of calculating the degree of ionisation in the case of mixtures. Let the solution contain 2.38 mg. equivalents of calcium sulphate and 6.33 of calcium bicarbonate. The ionisation was calculated from the conductivity as given in Landolt-Börnstein's tables, 3rd Ed., the ionisation of the bicarbonate being assumed to be the same as that of calcium chloride. Divide the water by trial between the two salts so that the solutions are approximately isohydric. Thus, 2.38 mg. equivalents of sulphate in 210 c.c. of water give a concentration of 11.33 mg. equivalents per litre, corresponding with ionisation of 0.622 and concentration of calcium ions 7.05 mg. equivalents per litre. The 6.33 mg. equivalents of bicarbonate dissolved in the rest of the water (790 c.c.) give a concentration of 8.01 mg. equivalents per litre, corresponding with ionisation 0.89 and

TABLE III.

Time.	H ₂ CO ₃ .	(Ca/2·HCO ₃).	Ionisation.	HCO ₃ .	CaSO ₄ .	Ionisation.	Calcium as sulphate.	Total calcium, 2Ca.	F.
43	1·04	4·89	0·91	4·45	2·382	0·642	1·53	5·98	114
16	1·81	6·08	0·895	5·44	2·382	0·630	1·50	6·94	113
43	2·06	6·33	0·89	5·63	2·382	0·622	1·48	7·11	109
16	3·15	7·25	0·88	6·38	2·382	0·60	1·43	7·81	101
43	4·55	8·83	0·88	7·77	2·382	0·59	1·40	9·17	121
16	6·56	9·85	0·872	8·59	2·382	0·585	1·39	9·98	112
—	3·562	7·00	0·875	6·12	6·25	0·579	3·62	9·74	102
—	4·94	7·58	0·897	6·80	12·50	0·545	6·81	13·61	127

The average value of F is 113, the same as in the absence of extraneous calcium salts.

Effect of Sodium Bicarbonate.—The same general law should hold good, but the solubility of the limestone should be reduced in a still greater measure, namely, inversely as the square of the total bicarbonate when the free carbonic acid is kept constant. The degree of dissociation of the sodium bicarbonate was assumed to be the same as that of calcium bicarbonate.

TABLE IV.

Time.	H ₂ CO ₃ .	(Ca/2·HCO ₃).	Ionisation.	HCO ₃ as calcium.	NaHCO ₃ .	Ionisation.	HCO ₃ as sodium.	Total HCO ₃ .	F.
54	4·75	5·57	0·869	4·84	6·25	0·869	5·43	10·27	107
54	4·06	3·40	0·850	2·89	12·50	0·85	10·62	13·51	130

Effect of Salts Containing no Common Ion with Calcium Bicarbonate.

The effect of sodium chloride, sodium sulphate, and magnesium sulphate was examined. These salts should somewhat increase the value of F , that is, the solvent action on calcium carbonate. This was found to be the case.

TABLE V

Salt.	Time.	H ₂ CO ₃ .	(Ca/2·HCO ₃).	Ionisation.	HCO ₃ .	F.
NaCl: 12·5 × 10 ⁻³	54	3·10	8·25	0·89	7·34	127
Na ₂ SO ₄ : 12·5 × 10 ⁻³	54	1·875	7·32	0·90	6·59	152
MgSO ₄ : 6·25 × 10 ⁻³	53	4·44	9·22	0·885	8·16	122
MgSO ₄ : 6·25 × 10 ⁻³	53	2·56	8·12	0·89	7·23	147

For ordinary fresh waters the effect of these salts on F is slight, but in mineral waters or sea-water it would have to be considered.

Value of the Constants.—The value of k_1 , the "solubility product" concentration of calcium ions 7·13 mg. equivalents per litre. The solutions are therefore approximately isohydric, and the degree of ionisation will not alter on mixing. Therefore, the ionisation of the sulphate in the original solution is 0·622, and of the bicarbonate, 0·89.

of calcium carbonate, could be calculated if k_2/k_3 were known. k_2 is known to be 3.04×10^{-7} from the experiments of Walker and McCormack. Bodländer has calculated k_3 from the experiments of Shields on the hydrolysis of sodium carbonate, but McCoy (*Amer. Chem., J.*, 1903, 29, 437) has pointed out that some error has crept into the calculations of Shields, so that Bodländer's value for k_3 , and hence for k_1 , is wrong. McCoy (*loc. cit.*) determined the value of k_2/k_3 directly. It increases very considerably on dilution, and was found to be 5300 for $N/10$ -solutions. McCoy assumes that it would become constant beyond this dilution, but we have found that this is not the case. We have extended McCoy's determinations to higher dilutions, and also repeated and amplified Shields' experiments, and prefer to leave the discussion of the value of k_1 until the publication of these results. In any case, the value of F should be proportional to k_1 for different forms of calcium carbonate, and should also be a function of the solubility of the carbonate in pure water. The "solubility product" cannot be inferred from the latter unless the degree of hydrolysis is known.

Since $k_1 = \text{Ca} \times \text{CO}_3$, we should, supposing no hydrolysis, have $\text{Ca} = \text{CO}_3$ and $k_1 = \text{Ca}^2$, where Ca is the concentration of the calcium in a saturated solution of the carbonate in pure water. But calcium carbonate is undoubtedly hydrolysed to a large extent according to the scheme: $\text{CaCO}_3 + 2\text{H}_2\text{O} = \text{Ca}(\text{HCO}_3)_2 + \text{Ca}(\text{OH})_2$. Here the concentration of the bicarbonate is equal to that of the hydrate, and we have the concentrations:

$$\text{Ca} = \text{CO}_3 + \frac{\text{HCO}_3}{2} + \frac{\text{OH}}{2},$$

or

$$\text{Ca} = \text{CO}_3 + \text{HCO}_3.$$

If the percentage of hydrolysis be $100x$, then $\text{HCO}_3 = x\text{Ca}$ and $\text{CO}_3 = (1-x)\text{Ca}$, so that $k_1 = \text{Ca} \times \text{CO}_3 = (1-x)\text{Ca}^2$. For different forms of calcium carbonate, say calcite and aragonite, x will be practically the same, since the solubilities are not widely different.

Let k_1 , Ca, and F apply to calcite, and k_1' , Ca', and F' to aragonite, then:

$$\frac{F'}{F} = \frac{k_1'}{k_1} = \frac{\text{Ca}'^2}{\text{Ca}^2} \quad \text{or} \quad \frac{\text{Ca}'}{\text{Ca}} = \sqrt{\frac{F'}{F}}.$$

Whatever the actual value of k_1 or of the hydrolysis, the square roots of F should be proportional to the solubilities of the two forms. We have tested this conclusion by experiments on calcite and aragonite under identical conditions.

TABLE VI.

Substance.	Time.	H ₂ CO ₃ .	(Ca/2·HCO ₃).	Ionis- ation.	HCO ₃ .	F.
Calcite	173	1.605	6.37	0.91	5.796	121.3
Aragonite	173	1.145	6.29	0.91	5.723	163.7

The ratio $\frac{F'}{F}$ is 1.35, and the square root, 1.162. According to Kohlrausch, the relative solubilities of aragonite and calcite are at 18° as 15 to 13, and the ratio, 1.154. The agreement is satisfactory. Evidently aragonite, being the more soluble form, must gradually pass into calcite if both forms are present.

Conclusions.

(1) The equilibrium between calcium carbonate and fresh waters is governed by the law :

$$\frac{\text{HCO}_3^2 \times \text{Ca}}{\text{H}_2\text{CO}_3} = F' \times 10^{-6},$$

where F' is a constant.

(2) The mean value of F' is about 113 for calcite. It is a criterion of the saturation of a water in contact with limestone, and may be called the "saturation factor" of the water. If less than 113, the water is not saturated, if over 113 it is supersaturated.

(3) This law has been verified in the presence of calcium chloride, calcium sulphate, sodium bicarbonate, sodium chloride, sodium sulphate, and magnesium sulphate in quantities such as occur in natural fresh waters. For mineral or sea-waters the factor would be increased.

(4) The law may be stated in familiar terms as follows, the hardness referred to being that produced by lime salts, and correction for ionisation being supposed. In general, when a water is in equilibrium with the limestone through which it percolates :

(a) The square of the alkalinity is directly as the free carbonic acid and inversely as the total hardness.

If there is no alkalinity or hardness except that due to the dissolved limestone, then :

(b) The cube of the temporary hardness (dissolved limestone) is directly as the free carbonic acid.

If permanent hardness (due to lime) is present, then :

(c) The square of the temporary hardness (dissolved limestone) is directly as the free carbonic acid and inversely as the total hardness.

If permanent hardness is absent and other bicarbonates are present, then :

(d) The hardness (dissolved limestone) is directly as the free carbonic acid and inversely as the square of the alkalinity.

(5) The constant F' is proportional to the "solubility product" of the solid calcium carbonate, and to the square of the solubility in pure water in the case of calcite and aragonite.

CLI.—*Double and Triple Ferrocyanides of Magnesium, Aluminium, and Cerium with Potassium and Ammonium.*

By FREDERIC WILLIAM ROBINSON.

THE object of this work was to ascertain which metals form double ferrocyanides with potassium, the nature, composition, and properties of these salts, and the effect of the presence of ammonium salts on their formation and composition. Further, in the case of triple salts, to determine whether they are definite salts, or whether the composition varies with the conditions under which they are prepared.

It has already been shown that, in the case of the double ferrocyanides of calcium, the presence of ammonium salts causes the precipitated salts to contain ammonium, but not in definite quantity (Campbell Brown, *Trans.*, 1907, 91, 1826), and the metals strontium and barium (Campbell Brown, *loc. cit.*), zinc and cadmium (Miller, *J. Amer. Chem. Soc.*, 1902, 24, 226, 823; 1904, 26, 952), and thallium (T. Fischer and Benzia, *Chem. Zeit.*, 1902, 26, 49) have also been previously investigated.

Preparation of Potassium Magnesium Ferrocyanide.

Equivalent quantities of cold concentrated solutions of potassium ferrocyanide and magnesium chloride were mixed. After a short time a white, microcrystalline precipitate was formed, which was collected, washed with cold water, and dried in a desiccator. Under the microscope the crystals were seen to consist of square plates, and these were not altered by drying or by heating to 120°.

The air-dried salt, after being heated for five hours at 105°, and then at 120° for two hours, lost no weight. The salt as precipitated is therefore anhydrous. When pure it is white, but, unless quite dry, soon becomes cream-coloured, owing, probably, to the action of atmospheric carbon dioxide. Gigli, in 1898 (*Chem. Zeit.*, 22, 866), showed that carbon dioxide decomposes aqueous solutions of ferrocyanides.

Solubility.—A saturated aqueous solution of the salt contains 1.95 grams per litre at 17°.

Analysis.—The method of analysis adopted was the same as that employed by Campbell Brown for the analysis of potassium calcium ferrocyanide (*loc. cit.*), namely, by treatment with lead chloride and estimating the magnesium and potassium in the filtrate from the lead ferrocyanide:

Found, Mg = 7.72 ; K = 24.45.

$K_2MgFeC_6N_6$ requires Mg = 7.64 ; K = 24.84 per cent.

Preparation of Ammonium Magnesium Ferrocyanide.

Ammonium ferrocyanide was mixed with a concentrated solution of magnesium chloride in equivalent proportion. Small, white crystals were obtained, having the same form as the potassium salt. The salt lost no water at 105° or 120°.

Solubility.—A saturated aqueous solution of the salt contains 2.48 grams per litre at 17°.

Analysis gave the following results :

Found, Mg = 8.68 ; NH_4 = 13.06.

$(NH_4)_2MgFeC_6N_6$ requires Mg = 8.92 ; NH_4 = 13.20 per cent.

Preparation of Triple Salts under Varying Conditions.

Precipitates were formed by mixing potassium ferrocyanide, magnesium chloride, and ammonium chloride in the proportions shown in the accompanying table.

The precipitated salt was in each case collected, washed with cold water, acetone, and ether, and kept in a desiccator.

The percentages of ammonium in these salts were determined. It was found that the proportion of ammonium to potassium in the precipitate varies with the amount of ammonium chloride present at the time of precipitation, but is not in the simple ratio of $NH_4 : K$ in the solution. When the proportion $NH_4 : K$ in the solution is less than about 1.7 : 1, the proportion $NH_4 : K$ in the precipitate is less than in the solution, but as this ratio approaches 2 : 1, the proportion of ammonium in the precipitate becomes greater than in the solution.

Table Showing Influence of Varying Proportions of Ammonium and Potassium on Composition of Salts.

Salt.	Mols. $MgCl_2$.	Mols. $K_4FeC_6N_6$.	Mols. NH_4Cl .	Ratio $NH_4 : K$ in initial solution.	Percentage $NH_4 : NH_4 + K$ in precipitate.	Percentage $NH_4 : NH_4 + K$ in initial solution.
A.....	1	1	1	1 : 4	13.9	20.0
B.....	1	1	2	1 : 2	25.4	33.3
C.....	1	1	4	1 : 1	45.3	50.0
D.....	1	1	8	2 : 1	68.1	66.6
E.....	1	1	20	5 : 1	86.2	83.3
F.....	1	2	20	5 : 1	87.0	83.3
G.....	1	1	6.8	1.7 : 1	63.1	63.0

As the time of precipitation might influence the composition of the precipitate, the salt *C* was collected fractionally. The solutions of potassium ferrocyanide and ammonium chloride were well mixed, and the magnesium chloride solution then added, the mixture being quickly stirred and kept for fifteen minutes. The precipitate was collected, and the filtrate kept for an hour, when the bulk of the precipitate had formed. After collecting this, the solution was kept overnight, when a further quantity of salt was precipitated. The fractions were called C_1 , C_2 , and C_3 .

As it was possible that these fractions were not equally soluble in water, they were washed with a mixture of equal parts of acetone and water, then with pure acetone, and finally with ether.*

The ammonium in these fractions was estimated, with the following results :

C_1 , $NH_4 = 4.63$,	equal to	38.9	per cent. of	$(NH_4)_2MgFeC_6N_6$.
C_2 , $NH_4 = 4.65$,	„	39.1	„	„
C_3 , $NH_4 = 4.83$,	„	40.6	„	„

When a large excess of ammonium chloride is present in the solution from which the salt is precipitated, ammonium begins to displace magnesium before it has displaced all the potassium. The salt *E* gave $Mg = 8.65$, $NH_4 = 11.41$, and $K = 3.47$ per cent., corresponding with 46.8 per cent. of $Mg_2FeC_6N_6$, 45.0 per cent. of $(NH_4)_4FeC_6N_6$, and 8.2 per cent. of $K_4FeC_6N_6$.

Salt *F*, prepared from the same proportions of ammonium chloride and potassium ferrocyanide, but with one-half the proportion of magnesium chloride as compared with *E*, gave $Mg = 8.60$, $NH_4 = 11.52$, and $K = 3.34$ per cent., corresponding with 46.5 per cent. of $Mg_2FeC_6N_6$, 45.4 per cent. of $(NH_4)_4FeC_6N_6$, and 8.1 per cent. of $K_4FeC_6N_6$.

Aluminium Salts.

Wyrouboff (*Ann. Chim. Phys.*, 1879, [v], 18, 446) described the preparation of aluminium ferrocyanide by mixing cold concentrated solutions of potassium ferrocyanide and alum, to which he assigned the formula $Al_4(FeC_6N_6)_3, 17H_2O$.

In order that the salt may be precipitated in a filterable form, it is necessary that a large quantity of electrolyte be present; the probability is that Wyrouboff prepared the salt in presence of excess of alum. Had he not done so he would have obtained a double salt, $KAlFeC_6N_6, xH_2O$, similar to the double salts which have been investigated by the present author.

* These salts are insoluble in a mixture of acetone and water, and in the time taken to filter off, the mixture does not precipitate any salts from the mother liquor, although it does so after some minutes.

Preparation of Potassium Aluminium Ferrocyanide.

N/2-Aqueous solutions of pure aluminium chloride and potassium ferrocyanide were mixed in molecular proportions, and, on keeping, the whole set to a stiff jelly. The preparation was therefore repeated, using *N*/4- and *N*/8-solutions, and in each case a similar result was obtained; the jelly did not settle, and passed easily through a filter paper. Other methods of precipitation were therefore tried. The double ammonium salt prepared in the same way was found to be a similar jelly. With the aid of a microscope, it was just possible to perceive the granular nature of the jelly.

The action of coagulants on the jelly was tried, but heat had no effect on it, and alcohol, acetone, ether, or other organic liquids did not flocculate it even on boiling.

The salts were also precipitated in presence of ions of high valency, alike positive and negative, but flocculation was not effected with either platinum tetrachloride or ammonium hydrogen phosphate.

When the potassium salt was prepared in presence of a large quantity of potassium chloride, it settled on standing, and could be filtered off by the aid of a pump. As, however, it was desirable to isolate the salts precipitated in presence of an amount of potassium or ammonium equivalent only to that required for the formation of the salt $\text{KAlFeC}_6\text{N}_6$, other methods were tried, and finally two were successfully employed.

Method I.—By means of a porous porcelain flask immersed in the jelly, the inside of the flask being connected to a filter pump, the salt could be slowly filtered off, and washed successively with water, alcohol, and ether. The dried salts are dark green in transparent masses, and when powdered are light bluish-green.

Method II.—The jelly was centrifugated at 3000 revolutions per minute, when the precipitate collected at the bottom of the tubes, leaving a clear liquid above, but the precipitate on suspension in distilled water did not settle again when centrifugated, so that it was impossible to wash the salt with water. It was therefore centrifugated after suspension in *N*-aqueous potassium thiocyanate, from which it readily settled, and again after suspension in acetone.*

Potassium thiocyanate is soluble in acetone, and the solution does not decompose the salt. After centrifugating with acetone, the salt was collected, washed with acetone and then ether, and dried in a vacuum.

* The suspension of the jelly in acetone is effected by rubbing in a mortar, but is a rather tedious operation.

Analysis.—A known weight of the salt was fused with potassium hydrogen sulphate, and the cooled product was dissolved in water, oxidised by nitric acid, and the mixed hydroxides of iron and aluminium precipitated by ammonia, calcined, and weighed. Iron was estimated volumetrically in the product of a separate fusion.

Analysis shows that the potassium salts isolated by centrifugation (I) and filtration (II) possess the same composition:

Found, (I) Fe = 15.36 ; Al = 7.95.

(II) Fe = 15.5 ; Al = 7.97.

$KAlFeC_6N_6 \cdot 4H_2O$ requires Fe = 16.0 ; Al = 7.72 per cent.

As indicated, the salts contain 4 molecules of water; this is lost at 100°.

The ammonium aluminium salt was also analysed:

Found, $NH_4 = 5.22$.

$NH_4AlFeC_6N_6 \cdot 4H_2O$ requires $NH_4 = 5.47$ per cent.

These salts therefore possess the composition: $RAlFeC_6N_6 \cdot 4H_2O$, where R is the alkali metal.

When anhydrous they have a deep blue colour, resembling that of Prussian-blue.

As the salts prepared in the presence of a large quantity of electrolyte could be readily filtered, the double salts were prepared by mixing concentrated solutions containing the molecular proportions of potassium ferrocyanide, aluminium chloride, and ammonium chloride indicated below, and the precipitates were washed with a mixture of equal parts of acetone and water, then with acetone, and finally with ether.

Salt.	$K_4FeC_6N_6$.	$AlCl_3$.	NH_4Cl .	KCl.
A	1	1	—	20
B	1	1	4	—
C	1	1	12	—

In the case of the potassium salt A, prepared in the presence of a large excess of potassium chloride, it was found that some of the aluminium had been displaced by potassium, the amount of aluminium found being only 6.20 per cent., approaching the value for



which requires Al = 5.8 per cent.

The triple salts, or mixed double salts, exhibit very similar phenomena to those observed in the case of the corresponding magnesium salts, as is shown by the following table.

Salt.	Percentage		Percentage
	$NH_4 : K$ in initial solution.	$NH_4 : NH_4 + K$ in initial solution.	$NH_4 : NH_4 + K$ in salt.
B	1 : 1	50	47.5
C	3 : 1	75	70.4

These results point to the fact that, as in the case of magnesium, the ammonium double salt is more soluble in water than that of potassium.

Thallium.

Attempts were made to prepare a double ferrocyanide of thallium and potassium of the formula $K_3TlFeC_6N_6$, but without success, the salt $Tl_4FeC_6N_6 \cdot 2H_2O$ always resulting. This salt was first prepared by Kuhlmann (*Compt. rend.*, 1862, 55, 607), who found that it was soluble in excess of potassium ferrocyanide, but he did not analyse it.

Lamy and Descloizeaux (*Compt. rend.*, 1868, 66, 1146) prepared the same salt, and assigned to it the formula $Tl_2FeC_3N_3 \cdot 2HO$. They found that it loses water at 100° . The salt has been found to crystallise in well-defined, yellow, quadratic pyramids, sparingly soluble in cold, but readily so in hot, water. It is stable in air, but loses its water of crystallisation on keeping over calcium chloride. A cold saturated solution of this salt in a $N/2$ -solution of potassium ferrocyanide was prepared and allowed to evaporate isothermally over sulphuric acid, when only the original salt, $Tl_4FeC_6N_6 \cdot 2H_2O$, was deposited.

Fischer and Benzián (*loc. cit.*) have also tried without success to prepare this double salt, but obtained one of the composition $K_4FeC_6N_6 \cdot K_3TlFeC_6N_6 \cdot 6H_2O$.

Cerium.

Preparation of Potassium Cerium Ferrocyanide.

Equivalent quantities of cold concentrated solutions of potassium ferrocyanide and pure cerium chloride (Kahlbaum's) were mixed, when a white salt was precipitated. This was collected, washed with water, and dried in the air. Under the microscope it appeared to be crystalline, but the shape of the crystals could not be determined.

When heated at 100° and finally at 120° , the salt lost no weight, and is therefore anhydrous.

Analysis.—A known weight of the cerium salt was fused with potassium hydrogen sulphate, the mass being then cooled and extracted with dilute hydrochloric acid. A small quantity of nitric acid was then added to oxidise ferrous salts, and, after cooling, the solution was rendered nearly neutral with ammonia and the cerium precipitated as oxalate by ammonium oxalate. The precipitate was collected, dried, ignited, and weighed as CeO_2 :

Found, $Ce = 35.6$.

$KCeFeC_6N_6$ requires $Ce = 35.8$ per cent.

The salt is therefore analogous to the potassium aluminium ferrocyanide already described.

Sodium and ammonium cerium ferrocyanides were also prepared, and were found to possess compositions analogous to that of the potassium cerium salt.

Sodium cerium ferrocyanide : Found, Ce = 36.9.

$\text{NaCeFeC}_6\text{N}_6$ requires Ce = 37.3 per cent.

Ammonium cerium ferrocyanide : Found, Ce = 38.4.

$\text{NH}_4\text{CeFeC}_6\text{N}_6$ requires Ce = 37.9 per cent.

Influence of the Presence of Ammonium Chloride on the Composition of the Precipitated Salt.

Precipitates were formed by mixing potassium ferrocyanide, cerium chloride, and ammonium chloride in the proportions shown in the accompanying table. The precipitated salt was in each case washed with a mixture of acetone and water, then with acetone, and finally with ether, and was kept in a desiccator.

The percentages of ammonium in these salts were determined, and were found to vary with the proportion $\text{NH}_4 : \text{K}$ in the original solution, but were not strictly proportional to it.

Salt.	Mols. CeCl_2 .	Mols. $\text{K}_4\text{FeC}_6\text{N}_6$.	Mols. NH_4Cl .	$\text{NH}_4 : \text{K}$ ratio in initial solution.	Percentage $\text{NH}_4 : \text{NH}_4 + \text{K}$ in precipitate.	Percentage $\text{NH}_4 : \text{NH}_4 + \text{K}$ in initial solution.
<i>A</i>	1	1	2	1 : 2	25.54	33.3
<i>B</i>	1	1	4	1 : 1	41.82	50.0
<i>C</i>	1	1	8	2 : 1	56.24	66.6
<i>D</i>	1	10	10	1 : 4	14.48	20.0

When the proportion of cerium to the alkali metals is small, as in the salts *C* and *D*, the same behaviour is observed as with magnesium and aluminium, namely, that the cerium is displaced by the alkali metals, tending to form the salt $(\text{R}_2\text{Ce})_4(\text{FeC}_6\text{N}_6)_5$, R being the alkali metal :

Salt *C* contains Ce = 33.2, and Salt *D*, Ce = 29.6.

$\text{KCeFeC}_6\text{N}_6$ requires Ce = 35.8 per cent.

$(\text{K}_2\text{Ce})_4(\text{FeC}_6\text{N}_6)_5$,, Ce = 29.0 ,,

It is seen, therefore, that the triple salts are really mixtures of double salts.

My best thanks are due to Prof. Campbell Brown for facilities for conducting this work, and for valuable help and suggestions during its progress.

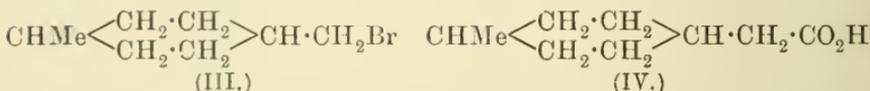
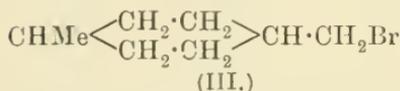
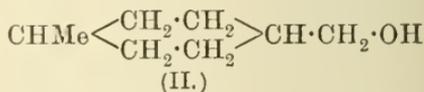
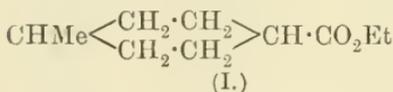
CLII.—*The Action of Bromocyclohexane and of 4-Bromo-1-methylcyclohexane on the Sodium Derivative of Ethyl Malonate.*

By EDWARD HOPE and WILLIAM HENRY PERKIN, jun.

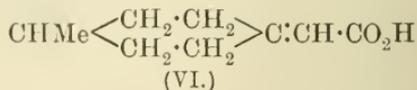
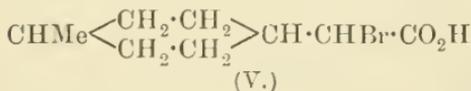
THIS investigation was commenced in the hope of finding a convenient method for the preparation of 1-methylcyclohexylidene-4-acetic acid,



The first synthesis of this acid was carried out in the following way (Perkin and Pope, *Trans.*, 1908, **93**, 1076): Ethyl 1-methylcyclohexane-4-carboxylate (I) was reduced by sodium and alcohol to 1-methylcyclohexylcarbinol (II); this was then converted into 1-methylcyclohexylcarbinyl bromide (III), from which 1-methylcyclohexyl-4-acetic acid (IV) was obtained by the action of potassium cyanide and subsequent hydrolysis.

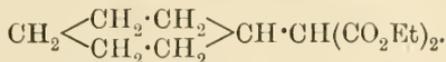


This acid was next converted, by the action of bromine, into α -bromo-1-methylcyclohexyl-4-acetic acid (V), the ester of which, on treatment with diethylaniline and subsequent hydrolysis, yielded 1-methylcyclohexylidene-4-acetic acid (VI).

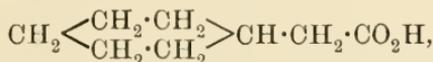


This process had many disadvantages. In the first place the number of operations which had to be carried out rendered the preparation a very laborious one, but the most serious drawback was the fact that the 1-methylcyclohexylidene-4-acetic acid ultimately obtained was far from pure. This was found to be due to the presence of considerable quantities of 1-methylcyclohexyl-4-acetic acid, the ester of which is produced during the action of diethylaniline on ethyl α -bromo-1-methylcyclohexyl-4-acetate by a process of reduction which is not

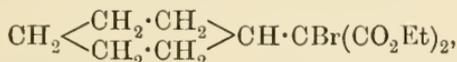
easily followed. In the present series of experiments the first step was the study of the action of bromocyclohexane on the sodium derivative of ethyl malonate, a decomposition which leads to the formation of *ethyl cyclohexylmalonate*,



This ester yields, on hydrolysis, *cyclohexylmalonic acid* (m. p. 176—178°), and this is decomposed at 180° into carbon dioxide and *cyclohexylacetic acid* (m. p. 29°),



Ethyl *cyclohexylmalonate* reacts readily with bromine with evolution of hydrogen bromide and formation of *ethyl α-bromocyclohexylmalonate*,



and *α-bromocyclohexylmalonic acid* (m. p. 149—151°) is readily obtained when the free acid is similarly treated.

Contrary to expectation, great difficulty was experienced in bringing about the elimination of hydrogen bromide from ethyl *α-bromocyclohexylmalonate*, such reagents as diethylaniline and pyridine producing secondary decompositions, which caused reduction and resulted in the formation of ethyl *cyclohexylmalonate*, whereas methyl-alcoholic potassium hydroxide yielded *ethyl α-methoxycyclohexylmalonate*,



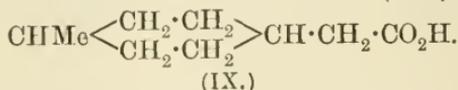
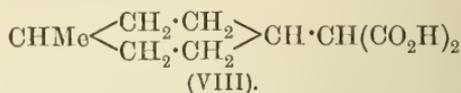
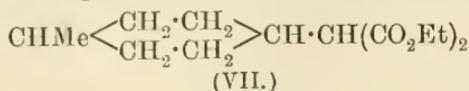
and sodium ethoxide the corresponding *ethoxy-derivative*.

When, however, the bromo-ester was digested with barium hydroxide, the decomposition proceeded with elimination of hydrogen bromide and formation of *cyclohexylideneacetic acid* (m. p. 90°), but even in this case some reduction took place, and the product contained *cyclohexylmalonic acid*.

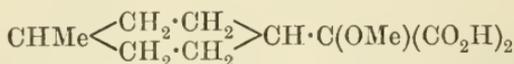
In the second series of experiments, we prepared *ethyl 1-methylcyclohexyl-4-malonate* (VII) from 4-bromo-1-methylcyclohexane by the action of the sodium derivative of ethyl malonate, and from this, by hydrolysis, *1-methylcyclohexyl-4-malonic acid* (VIII), which melts at 177—178° with elimination of carbon dioxide and formation of *1-methylcyclohexyl-4-acetic acid* (m. p. 73°; IX), which had already been prepared by Perkin and Pope (*Trans.*, 1908, 93, 1079) by a different process.

In the hope of converting ethyl *1-methylcyclohexyl-4-malonate*, or the free acid, into *1-methylcyclohexylidene-4-acetic acid*, we prepared the bromo-derivatives of these substances and treated them with

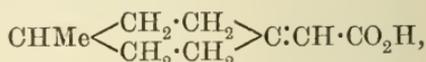
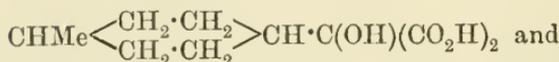
diethylaniline and pyridine under different conditions, but in all cases a complicated process took place, with formation of considerable



quantities of 1-methylcyclohexyl-4-acetic acid, and we were unable to isolate the unsaturated acid from the product of any of these reactions. Treatment with methyl-alcoholic potassium hydroxide converted the bromo-ester into *α-methoxy-1-methylcyclohexylmalonic acid*,

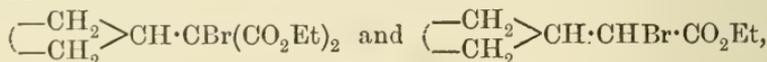


(compare p. 1368). When, however, ethyl *α*-bromo-1-methylcyclohexyl-4-malonate was hydrolysed with barium hydroxide, it was readily decomposed, with formation of 1-methylcyclohexyl-4-tartronic acid and 1-methylcyclohexylidene-4-acetic acid,



but the yield of the latter acid was quite unsatisfactory.

The most remarkable point in connexion with this and previous researches on the same subject is the difficulty which has been experienced in eliminating hydrogen bromide from *α*-bromo-esters of the types:



that is, containing a closed ring, whereas it is well known that this process takes place with great ease in the case of open-chain *α*-bromo-esters. Thus, for example, ethyl *α*-bromo*isovalerate*,



is very readily converted into ethyl dimethylacrylate, $\text{CMe}_2 : \text{CH} \cdot \text{CO}_2\text{Et}$, when it is digested with diethylaniline.

It is fortunate that, owing to the elegant method of formation recently devised by Wallach (*Annalen*, 1909, 365, 263), 1-methylcyclohexylidene-4-acetic acid may now be prepared in considerable quantities with comparative ease.

EXPERIMENTAL.

Ethyl cycloHexylmalonate.

The bromocyclohexane required for the synthesis of this substance is readily prepared by heating a mixture of *cyclohexanol* (100 grams) with acetic-hydrobromic acid (200 grams, saturated at 0°) for half an hour on the water-bath. The product is poured into water, the heavy oil extracted with ether, the ethereal solution washed with water and then with sodium carbonate until free from acetic acid, dried, and distilled, when almost the whole quantity passes over at 113—116°/150 mm., and consists of bromocyclohexane mixed with small quantities of unchanged *cyclohexanol*.

The preparation of ethyl *cyclohexylmalonate* is carried out as follows: Sodium (8.7 grams) dissolved in alcohol (150 c.c.) is well-cooled, mixed with ethyl malonate (60 grams) and bromocyclohexane (62 grams), and the whole heated on the water-bath for twenty-four hours. After adding water, the product is extracted with ether, the ethereal solution well washed, dried, evaporated, and the residue repeatedly distilled under diminished pressure, when, after an oil of low boiling point, consisting chiefly of *cyclohexene*, *cyclohexanol*, and ethyl malonate, has passed over, a considerable fraction is obtained distilling constantly at 163—165°/20 mm.:

0.1777 gave 0.4193 CO₂ and 0.1438 H₂O. C = 64.3; H = 9.0.

C₁₃H₂₂O₄ requires C = 64.4; H = 9.1 per cent.

Ethyl cyclohexylmalonate is a colourless, viscid oil, and is obtained in the above process in a yield of about 33 per cent. of that theoretically possible. Although it probably yields a sodium derivative, attempts to introduce a second *cyclohexyl* group by treating the pure ester with sodium ethoxide and bromocyclohexane gave a negative result.

cycloHexylmalonic Acid and cycloHexylacetic Acid.

The hydrolysis of ethyl *cyclohexylmalonate* takes place readily when the ester is digested with a slight excess of methyl-alcoholic potassium hydroxide on the water-bath, and, after one hour, the crystalline *potassium* salt which will have separated is collected, dissolved in water, and acidified with hydrochloric acid.

The solid acid is well washed and crystallised from formic acid, from which it separates in long, glistening prisms:

0.1242 gave 0.2653 CO₂ and 0.0866 H₂O. C = 58.2; H = 7.7.

C₉H₁₄O₄ requires C = 58.0; H = 7.5 per cent.

cycloHexylmalonic acid melts at 176—178° and decomposes into

carbon dioxide and *cyclohexylacetic acid*; it is moderately readily soluble in warm water, and separates on cooling in small prisms. It is readily soluble in ether, slightly so in chloroform, and almost insoluble in benzene or light petroleum. The basicity of this acid was determined by titration with *N*/10-sodium hydroxide, when 0.362 gram neutralised 0.0146 NaOH, whereas this amount of a dibasic acid, $C_9H_{14}O_4$, should neutralise 0.0153 NaOH.

If the pure acid is heated at 180° , a vigorous evolution of carbon dioxide takes place, and when this has ceased, the residual, nearly pure *cyclohexylacetic acid* solidifies, and may be purified by crystallisation from formic acid:

0.1700 gave 0.4175 CO_2 and 0.1529 H_2O . C = 66.9; H = 9.9.

$C_8H_{14}O_2$ requires C = 67.6; H = 9.8 per cent.

cycloHexylacetic acid separates from formic acid in ill-defined plates, and, after pressing on porous porcelain and drying over sulphuric acid, the acid melts at about $28-29^\circ$.

α -Bromocyclohexylmalonic Acid.

This acid is best prepared by adding bromine (0.4 c.c.) to a solution of *cyclohexylmalonic acid* (1 gram) in carefully dried ether.

After remaining for four hours, the solution is warmed for a short time on the water-bath and the ether allowed to evaporate at the ordinary temperature, when a solid residue is obtained which crystallises from formic acid in magnificent rhombic plates:

0.1385 gave 0.0970 AgBr. Br = 29.8.

$C_9H_{13}O_4Br$ requires Br = 30.2 per cent.

α -Bromocyclohexylmalonic acid melts at $154-156^\circ$, and is very soluble in ether, moderately so in chloroform, and very sparingly so in water or benzene.

Considerable quantities of ethyl *α -bromocyclohexylmalonate* were prepared by adding bromine (4.7 c.c.), drop by drop, to pure ethyl *cyclohexylmalonate* (21 grams) at the ordinary temperature.

The bromine was rapidly absorbed, with the evolution of hydrogen bromide, and, after remaining for three hours, the whole was dissolved in ether, the ethereal solution washed with dilute sodium carbonate, dried, evaporated, and the residual syrup fractionated under diminished pressure:

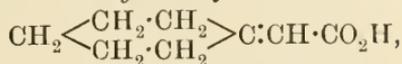
0.1234 gave 0.0736 AgBr. Br = 25.4.

$C_{13}H_{21}O_4Br$ requires Br = 24.9 per cent.

Ethyl α -bromocyclohexylmalonate distils at $183-185^\circ/20$ mm.

*Attempts to Eliminate Hydrogen Bromide from
Ethyl α -Bromocyclohexylmalonate.*

These experiments were undertaken with the object of determining the conditions under which *cyclohexylideneacetic acid*,



is produced from ethyl α -bromocyclohexylmalonate.

I. *The Action of Diethylaniline and of Pyridine.*—In the first experiment the bromo-ester (15 grams) was added to boiling diethylaniline (25 grams), and, after continuing the boiling for four hours, the dark opaque liquid was cooled, poured into dilute sulphuric acid, and extracted with ether. The dark ethereal solution was washed with dilute sodium carbonate, dried, evaporated, and the residue distilled, when a small quantity of oil was obtained boiling at 155—165°/20 mm. This, on hydrolysis with methyl-alcoholic potassium hydroxide, yielded an acid melting at 175—176°, which, on examination, proved to be *cyclohexylmalonic acid*. In a second experiment, the same quantities were heated at 120° for five hours, when the product was found to consist of about two-thirds unchanged bromo-ester and tarry matter, from which nothing definite could be isolated.

The bromo-ester (20 grams) was next digested with pyridine (80 c.c.) for five hours on the water-bath, when the product, extracted in the usual manner, distilled at 180—185°/20 mm., and consisted of unchanged bromo-ester, almost the whole quantity being recovered. When the experiment was repeated at the boiling temperature for six hours, about 40 per cent. of the bromo-ester was recovered, and the remainder consisted principally of uninviting tarry matter.

II. *The Action of Potassium Hydroxide.*—Ethyl α -bromocyclohexylmalonate is scarcely attacked by boiling with 30 per cent. aqueous potassium hydroxide, but weaker alkali gradually decomposes it, with the formation of considerable quantities of *cyclohexylmalonic acid*.

When the bromo-ester (23 grams) was digested with a strong solution of potassium hydroxide (40 grams) in methyl alcohol, potassium bromide soon separated, but the potassium salt of the organic acid remained dissolved in the alcohol. In order to isolate this acid, the product was evaporated to dryness, the residue powdered, suspended in alcohol, and saturated with hydrogen chloride, and, after remaining for several hours, water was added and the ester extracted with ether.

The ethereal solution was washed with sodium carbonate, which removed considerable quantities of an acid-ester, and the latter was again esterified. The combined esters were then fractionated, when

a considerable quantity of an oil was obtained, which distilled at about $165^{\circ}/20$ mm., and evidently consisted of *ethyl α -methoxycyclohexylmalonate* :

0.2144 gave 0.4890 CO_2 and 0.1678 H_2O . C = 62.2 ; H = 8.7.

0.2006 ,, 0.4548 CO_2 ,, 0.1524 H_2O . C = 61.7 ; H = 8.4.

$\text{C}_{14}\text{H}_{24}\text{O}_5$ requires C = 61.7 ; H = 8.8 per cent.

On hydrolysis with alcoholic potassium hydroxide, this ester yielded a syrupy acid, which was not further investigated.

The nature of this change was confirmed by the investigation of the action of sodium ethoxide on ethyl α -bromocyclohexylmalonate.

The bromo-ester (16 grams) was poured into a solution of sodium (3.5 grams) in alcohol (45 c.c.), when immediate decomposition took place, the liquid became quite warm, and a yellow solid separated.

After heating for half an hour on the water-bath, the product was isolated in the usual manner and fractionated, when almost the whole quantity distilled at about $165^{\circ}/20$ mm., and evidently consisted of *ethyl α -ethoxycyclohexylmalonate* :

0.1704 gave 0.4016 CO_2 and 0.1379 H_2O . C = 64.3 ; H = 9.0.

$\text{C}_{16}\text{H}_{28}\text{O}_5$ requires C = 64.0 ; H = 9.3 per cent.

III. *The Action of Barium Hydroxide. Formation of cyclohexylideneacetic Acid.*—In this experiment ethyl α -bromocyclohexylmalonate (15 grams) was digested with a strong aqueous solution of barium hydroxide (45 grams) for five hours. The product was kept until cold, filtered from excess of barium hydroxide, mixed with ice, and acidified, when an immediate separation of needle-shaped crystals took place. The precipitate was collected, washed, recrystallised from dilute methyl alcohol, and analysed, with the following result :

0.1434 gave 0.3616 CO_2 and 0.1158 H_2O . C = 68.8 ; H = 8.9.

$\text{C}_8\text{H}_{12}\text{O}_2$ requires C = 68.6 ; H = 8.6 per cent.

This acid melted at 89 — 90° , and proved, on examination, to be cyclohexylideneacetic acid, since when mixed with a sample of this acid which had been obtained by another process (Wallach, *Annalen*, 1909, 365, 261), there was no alteration in melting point.

The aqueous liquors from which this acid had separated yielded, on extraction with ether, an oily acid, which gradually solidified, and after crystallisation, first from formic acid and then from water, melted at 175 — 176° and consisted of cyclohexylmalonic acid :

0.1394 gave 0.2937 CO_2 and 0.0937 H_2O . C = 57.5 ; H = 7.4.

$\text{C}_9\text{H}_{14}\text{O}_4$ requires C = 58.0 ; H = 7.5 per cent.

1-Methylcyclohexyl-4-malonic Acid and its Derivatives.

Since the experiments on the preparation, properties, and decompositions of this acid were carried out on the same lines as those described in detail in the case of *cyclohexylmalonic acid*, it will only be necessary to refer to them briefly.

4-Bromo-1-methylcyclohexane was prepared by the action of acetic-hydrobromic acid on 1-methyl-4-cyclohexanol, and distilled at 124—126°/150 mm. In preparing ethyl 1-methylcyclohexyl-4-malonate, ethyl malonate (80 grams), mixed with sodium (11.6 grams) dissolved in alcohol (200 c.c.), was digested with bromomethylcyclohexane (90 grams), and the product isolated in the usual manner. It distilled at 163—165°/20 mm., and gave, on analysis, the following result:

0.1924 gave 0.4612 CO₂ and 0.1672 H₂O. C = 65.3; H = 9.6.

C₁₄H₂₄O₄ requires C = 65.6; H = 9.6 per cent.

When this ethereal salt was hydrolysed with methyl-alcoholic potassium hydroxide, it yielded a sparingly soluble *potassium* salt, from which the free acid was obtained by acidifying with hydrochloric acid:

0.1395 gave 0.3038 CO₂ and 0.0998 H₂O. C = 59.4; H = 7.9.

C₁₀H₁₆O₄ requires C = 60.0; H = 8.0 per cent.

The basicity was determined by titration with *N*/10-sodium hydroxide, when 0.244 gram neutralised 0.0972 NaOH, whereas this amount of a dibasic acid, C₁₀H₁₆O₄, should neutralise 0.0976 NaOH.

1-Methylcyclohexyl-4-malonic acid melts at 177—178°, and decomposes into carbon dioxide and 1-methylcyclohexyl-4-acetic acid; the latter separated from formic acid in pearly plates, melted at 73°, and was identical with the acid of this constitution which Perkin and Pope (*Trans.*, 1908, 93, 1075) had prepared by a different method. In preparing ethyl α -bromo-1-methylcyclohexyl-4-malonate, ethyl 1-methylcyclohexyl-4-malonate (20 grams) was gradually treated with pure bromine (4.2 c.c.), and, as soon as the reaction was complete, the product was extracted with ether, the ethereal solution washed with sodium carbonate, dried, and distilled, when almost the whole quantity passed over at 182—185°/20 mm. as a viscid, colourless syrup:

0.1330 gave 0.0758 AgBr. Br = 24.2.

C₁₄H₂₃O₄Br requires Br = 23.9 per cent.

α -Bromo-1-methylcyclohexyl-4-malonic acid was obtained by the action of bromine on the pure acid, and separated from formic acid in glistening prisms melting at 149—151°:

0.1183 gave 0.0800 AgBr. Br = 28.7.

C₁₀H₁₅O₄Br requires Br = 28.7 per cent.

Attempts to Eliminate Hydrogen Bromide from Ethyl α -Bromo-1-methylcyclohexyl-4-malonate.

When this bromo-ester was treated with diethylaniline or pyridine under the conditions described in the case of ethyl α -bromocyclohexylmalonate (p. 1365), much tarry matter was produced, and the only definite substance which could be isolated was ethyl 1-methylcyclohexyl-4-malonate. The bromo-ester reacts readily with methyl-alcoholic potassium hydroxide at the temperature of the water-bath, yielding potassium bromide and a sparingly soluble *potassium* salt, and, when this salt is acidified, a gum separates, which doubtless consists of α -methoxy-1-methylcyclohexyl-4-malonic acid, but as it did not solidify, the whole was esterified with alcohol and hydrochloric acid (compare p. 1365) and the ester fractionated. The oil distilling at about 168—173°/20 mm. consists of *ethyl α -methoxy-1-methylcyclohexyl-4-malonate*:

0.1571 gave 0.3640 CO₂ and 0.1235 H₂O. C = 63.2; H = 8.7.

0.2158 „ 0.5010 CO₂ „ 0.1726 H₂O. C = 63.3; H = 8.8.

C₁₅H₂₆O₅ requires C = 62.9; H = 9.1 per cent.

The Action of Barium Hydroxide on Ethyl α -Bromo-1-methylcyclohexyl-4-malonate.—As this action proceeds in a different manner from the corresponding decomposition of ethyl α -bromocyclohexylmalonate (p. 1366), it is necessary to describe it in detail.

The bromo-ester (15 grams) was boiled for five to six hours with a strong solution of barium hydroxide (45 grams), when a sparingly soluble *barium* salt gradually separated. This was collected, decomposed by hydrochloric acid, and extracted with ether, when a syrupy acid was obtained, which, over sulphuric acid in a vacuum desiccator, partly crystallised. In contact with porous porcelain the oily portion was readily absorbed, leaving a colourless, crystalline residue, which separated from formic acid in rhombic plates, and consisted of *1-methylcyclohexyl-4-tartronic acid*:

0.1267 gave 0.2567 CO₂ and 0.0849 H₂O. C = 55.2; H = 7.4.

C₁₀H₁₆O₅ requires C = 55.5; H = 7.4 per cent.

The constitution of this acid was demonstrated by heating it at 160°, when it decomposed with elimination of carbon dioxide and formation of a mixture of α -hydroxy-1-methylcyclohexyl-4-acetic acid and 1-methylcyclohexylidene-4-acetic acid. The product was distilled in a current of steam and the residue extracted with ether, when a solid acid was obtained, which, after crystallisation from formic acid, melted at 143°, and was identical with α -hydroxy-1-methylcyclohexyl-4-acetic acid described by Perkin and Pope (Trans., 1908, 93, 1075):

0.1196 gave 0.2725 CO₂ and 0.0979 H₂O. C = 62.1 ; H = 9.1.

C₉H₁₆O₃ requires C = 62.8 ; H = 9.3 per cent.

The steam distillate (and also the soluble barium salt from the hydrolysis described above) contained an oily acid, which, although it did not solidify, evidently consisted largely of 1-methylcyclohexylidene-4-acetic acid. This was shown by analysis and by the fact that, when oxidised by permanganate, it yielded considerable quantities of 1-methyl-4-cyclohexanone, which was easily identified by its general properties and by the melting point of its semicarbazone.

THE SCHUNCK LABORATORY,
THE UNIVERSITY,
MANCHESTER.

CLIII.—*The Hydrolysis of Amygdalin by Acids.* *Part I.*

By J. WALLACE WALKER and VERNON K. KRIEBLE.

ALTHOUGH this subject has been studied by several investigators, and varying results have been obtained according to the different experimental conditions employed, we find that, as yet, no completely systematic examination has been made, and consequently have commenced to carry it out in detail. The fact that amygdalin, when heated with dilute aqueous solutions of the strong acids, yields the same products as when treated with emulsin, namely, dextrose, benzaldehyde, and hydrocyanic acid, was first established by Ludwig (*Jahresb.*, 1855, 699). In a comparatively recent communication, Caldwell and Courtauld (*Trans.*, 1907, **91**, 666) have shown that this change involves a succession of reactions, the first of which consists in the hydrolytic elimination of one molecule of dextrose, and they have succeeded in isolating Fischer's *l*-mandelonitrile glucoside as an intermediate product, thus showing that the first point of the amygdalin molecule, C₆H₅·CH(CN)·O·C₆H₁₀O₅·C₆H₁₁O₅, to be attacked by dilute hydrochloric acid is the biose junction, just as when maltase is employed as hydrolyst (Fischer, *Ber.*, 1895, **28**, 1508). There are, however, two other points in the molecule of amygdalin susceptible of hydrolysis, namely, the junction between the biose and the mandelonitrile groups, and also the nitrile group itself. The well-known formation of *l*-mandelic acid when concentrated hydrochloric acid is substituted for dilute, might therefore be assumed to indicate an entirely different behaviour on the part of the

concentrated acid, or it might mean that both dilute and concentrated acids act similarly at first, hydrolysing amygdalin to dextrose and *l*-mandelonitrile, but differ in their subsequent action on this substance, the latter hydrolysing it further to ammonium chloride and *l*-mandelic acid, whilst the former decomposes it to benzaldehyde and hydrocyanic acid. The conclusion was, however, deduced by one of us (Walker, *Trans.*, 1903, **83**, 472) that the first point attacked by concentrated hydrochloric acid (D 1.1) is the nitrile group, which suffers hydrolysis to carboxyl, the elimination of the dextrose groups taking place subsequently. The entire course of the decomposition of the amygdalin molecule is thus different, according as weak or concentrated hydrochloric acid is employed as hydrolyst.

The above conclusion suggested the advisability of examining the behaviour of other strong acids in aqueous solution, for, although no difference in their action was to be anticipated on theoretical grounds, the same might be said of a single acid, such as hydrochloric, when employed at different concentrations. Although the statement that all concentrated acids behave alike in this respect has been generally accepted, it appears to be based entirely on analogy, for we cannot find that anyone has examined the behaviour of any acid other than hydrochloric acid. Experimentally, we find that a concentrated aqueous solution of sulphuric acid behaves in a totally different manner from one of hydrochloric acid, inasmuch as the former shows very little tendency to attack the nitrile group, which, as already stated, is the first point attacked by the latter. So slight indeed is this tendency that a large amount of *l*-mandelonitrile separates from the solution as an oil, and it seems to be only very slowly acted on further. Dilute sulphuric acid shows points of resemblance both with dilute hydrochloric acid and with concentrated sulphuric acid, inasmuch as it first removes one molecule of dextrose, producing Fischer's *l*-mandelonitrile glucoside, and then liberates *l*-mandelonitrile, on which it acts very slowly. Oxalic acid probably behaves mainly in the same way as dilute hydrochloric acid. Trichloroacetic acid has thus far only been examined in fairly concentrated solutions. Its behaviour is entirely anomalous, for it does not appear to effect the hydrolysis of amygdalin at all under conditions which enable hydrochloric acid to act fairly rapidly.

EXPERIMENTAL.

Hydrolysis by Dilute Hydrochloric Acid.—The hydrolytic action of normal acid has been quantitatively studied by Caldwell and Courtauld (*loc. cit.*). They have shown that at temperatures of

60° and 80° the junction of the two dextrose groups is first attacked with the formation of dextrose and Fischer's *l*-mandelonitrile glucoside, which on further hydrolysis yields a second molecule of dextrose and the decomposition products of *l*-mandelonitrile, namely, benzaldehyde and hydrocyanic acid.

Hydrolysis by Concentrated Hydrochloric Acid.—The action of concentrated hydrochloric acid solution (D 1.1) on *l*-amygdalin, *r*-amygdalin, and *r*-amygdalinic acid at 20° was examined by one of us (*loc. cit.*), the accompanying change of rotation being followed polarimetrically. In the case of *l*-amygdalin there was a large and rapid increase of lævoration, followed by a much slower but greater decrease, whereas *r*-amygdalin showed practically no change during the first period, but an equal diminution of lævoration during the second. There are three possible initial paths by which the hydrolysis may proceed, namely:

- (a) Amygdalin \rightarrow mandelonitrile + biose,
 - (b) Amygdalin \rightarrow mandelonitrile glucoside + dextrose,
- and (c) Amygdalin \rightarrow amygdalinic acid + ammonia.

Of these three, (b) is at once excluded by the observed large initial increase of lævoration when using *l*-amygdalin, since *l*-mandelonitrile glucoside has a smaller lævoration than that substance. Finally, (c) was indicated as the path selected by observing the behaviour of *r*-amygdalinic acid when similarly hydrolysed. Its rotatory power changed in a manner corresponding with the second period of *r*-amygdalin. Attempts to isolate the *l*-amygdalinic acid having been unsuccessful, the hydrolysis by concentrated hydrochloric acid has been further studied with different concentrations of acid and at different temperatures, and confirmation of the above conclusion has been sought and obtained in other ways. A solution was prepared containing 10 grams of *l*-amygdalin in 50 c.c. of hydrochloric acid (D 1.118), and allowed to reach the condition of maximum lævoration. It was then extracted with benzene, but gave no trace of *l*-mandelonitrile. The acid solution was then neutralised with sodium hydroxide to decompose any possible compound of hydrochloric acid with the nitrile, and again extracted with benzene, but no mandelonitrile was obtained on evaporation of the benzene. A similar solution, after attaining the maximum activity, was diluted with sufficient water to reduce the strength of the hydrochloric acid to normal, and then heated for eight hours in a closed vessel on the boiling-water bath. Neither benzaldehyde nor hydrocyanic acid could be detected in it after this treatment. These experiments prove conclusively that the hydrolysis does not take place according to (a). In the former communication the change of

rotation was not followed far past the maximum point, consequently there was no evidence obtained of the subsequent course of the hydrolysis of the *l*-amygdalinic acid, which may proceed by one of two paths, either:

(*d*) *l*-Amygdalinic acid \rightarrow *l*-mandelic acid + biose,

or (*e*) *l*-Amygdalinic acid \rightarrow *l*-mandelic acid glucoside + dextrose.

To gain information on this point, a series of observations have been made, covering the whole time of action or the major part of it. Some of the results obtained are given in the following tables. The material employed in (I) was Kahlbaum's, having the composition $C_{20}H_{27}O_{11}N, 2H_2O$, that in (II) and (III) had been recrystallised from water and had the composition $C_{20}H_{27}O_{11}N, 3H_2O$. In comparing the maximum rotation attained in (I) with those in (II) and (III), the former must therefore be multiplied by 493/511. Each solution contained 10 grams of material in 50 c.c., and was examined in the 2-dcm. tube:

TABLE I.

Temperature 28°. Hydrolyst: Hydrochloric acid (D 1.089).

Time in hours.	α_D .	Time in hours.	α_D .
0.5	-13.5°	90	-38.5°
3.75	15.4	97	39.22
18.25	24.34	115	39.88
24.5	26.5	140	39.14
42.0	32.1	161	39.14
67.0	36.4	186	38.0
72.0	36.9		

TABLE II.

Temperature 28°. Hydrolyst: Hydrochloric acid (D 1.118).

Time in hours.	α_D .	Time in hours.	α_D .
0.16	-15.0°	23.16	-39.10°
2.52	27.3	29.9	36.4
5.1	35.1	39.17	32.86
9.33	40.4	43.0	31.4
11.75	41.8	52.25	28.0
12.16	41.9	55.50	27.0
14.0	41.5	72.75	22.3
18.0	40.4	84.0	19.7

TABLE III.

Temperature 60°. Hydrolyst: Hydrochloric acid (D 1.118).

Time in minutes.	α_D .	Time in minutes.	α_D .
3	-14.3°	56	-17.7°
11	19.2	68	15.7
16	21.9	83	12.00
21	22.4	96	9.0
29	22.7	115	6.3
37	21.4	135	4.3
45	19.7	175	2.0

The observations in table III, where the hydrolysis has been carried to completion, do not, even when plotted in the form of a curve, show a separation into the three distinct reactions which must take place, consequently two of them must proceed with approximately the same velocity. Experiments were therefore made to determine the amount of chemical change which had taken place corresponding with definite changes in optical power. The solutions employed contained 10 grams of the compound $C_{20}H_{27}O_{11}N, 2H_2O$ in 50 c.c., and the diluent was hydrochloric acid (D 1.118). In the first experiment, the rotation was $\alpha_D -30.25^\circ$ after the solution had remained at 35° for ninety-six minutes, and it was found to contain reducing sugar equivalent to 8 per cent. of the total quantity of dextrose which 10 grams of amygdalin could yield. A portion of it, after neutralisation with sodium hydroxide, was heated for twenty-two hours at 40° with emulsin, and the liberated hydrocyanic acid was titrated with $N/50$ -iodine solution in order to determine how much remained as cyanogenetic glucoside. It was found that only 8 per cent. of the hydrocyanic acid, corresponding with 10 grams of amygdalin, was thereby liberated. Up to this point, therefore, the reaction had consisted mainly in the production of *l*-amygdalinic acid, although the formation of some reducing sugar shows that another slower reaction is proceeding contemporaneously. In a second experiment, the rotation in the 2-dcm. tube after the solution had remained at 38.5° for 230 minutes was -35.9° , and this was the maximum reading attained at that temperature. Estimations similar to the above showed that the solution now contained reducing sugar equivalent to 21 per cent. of the total quantity of dextrose obtainable from 10 grams of amygdalin, and that there still remained 5 per cent. of the amygdalin as a cyanogenetic glucoside. These observations, while confirming the conclusion regarding the first action of hydrochloric acid in producing *l*-amygdalinic acid, are not in themselves decisive as to whether a biose is liberated or not in the second stage. If liberated, however, it must be very strongly *l*ævorotatory to account for the great observed increase of *l*ævorotation as the reducing sugar increases in amount, but, since there is no corresponding increase of *l*ævorotation during the hydrolysis of *r*-amygdalinic acid under the same conditions, it follows that biose is not liberated, and consequently that (c) and (e) represent the course of the hydrolysis. The point of maximum optical activity of the solution, however, does not correspond with that of maximum content of *l*-amygdalinic acid, and the difficulty which, as already stated, was experienced in our attempts to isolate that substance by stopping the hydrolysis at the point of

maximum optical effect is thus entirely explained, for the solution then contains, besides that acid, an amount of free dextrose and of *l*-mandelic acid glucoside equivalent to 42 per cent. of the amygdalin employed. It is also evident, from the above tables, that the change in the velocity of the reaction for a comparatively small change in the concentration of the hydrolyst is very great. The concentrations of hydrochloric acid in the two experiments at 28° are in the ratio of 10 to 13, but the more dilute solution takes ten times longer to reach its maximum. Further, the maximum rotation attained is highest at low temperatures and with stronger acid, but whether this points to a change in the relative velocities of the several reactions has not yet been determined.

Hydrolysis by Concentrated Aqueous Solutions of Sulphuric Acid.—A solution containing 40 grams of sulphuric and 20 grams of amygdalin in 60 grams of water was heated on the water-bath to 90°. After a quarter of an hour it had become turbid, and on heating for an hour longer a layer of dark oil was found floating on its surface. This was extracted with benzene, and found to be strongly dextrorotatory in that solvent. On evaporation of the benzene there remained 4.573 grams of oil without any odour of benzaldehyde. The theoretical yield of mandelonitrile is 5.4 grams. On cooling, it crystallised and melted a little above 20°. It was hydrolysed by heating with concentrated hydrochloric acid solution, and evaporated to dryness on the water-bath. The mandelic acid was extracted from the residue with ether, and the ammonium chloride collected. It weighed 1.823 grams instead of the theoretical 1.8395 grams. The oil was therefore nearly pure *l*-mandelonitrile, and was obtained in 85 per cent. yield. The aqueous sulphuric acid solution was twice extracted with ether, and gave 0.8 gram of mandelic acid, which showed $[\alpha]_D - 74^\circ$. It had therefore been racemised to a considerable extent. This experiment shows that the first point in the amygdalin molecule attacked by a concentrated aqueous solution of sulphuric acid is totally different from that acted on by concentrated hydrochloric acid; in fact, what the one attacks first the other attacks last, and apparently with difficulty. In a second experiment a lower concentration of sulphuric acid was employed. On heating 10 grams of amygdalin with 50 c.c. of 2.77*N*-sulphuric acid to 98° for three hours, a dark oil separated, which was extracted with benzene. This solution, having a volume of 50 c.c., showed a rotation of $\alpha_D + 1.1^\circ$ in the 1-dcm. tube, and left on evaporation of the benzene 1.75 grams of oil, which was shown, as before, to be *l*-mandelonitrile. From the above data its specific rotation in benzene

solution is approximately $[\alpha]_D + 31.4^\circ$. The yield in this instance was only 65 per cent.

Hydrolysis by Dilute Aqueous Sulphuric Acid.—The strength of sulphuric acid employed in the three following experiments was 1.0135*N*. A solution containing 2 grams of amygdalin in 10 c.c. of this acid, after heating at 98° for three hours, remained quite clear when cooled. When heated at the same temperature for one hour longer it became milky when cold, and, after two hours' further heating, there were beads of oil floating on the solution, and it had acquired a distinct odour of oil of bitter almonds. A similar solution was heated at 98° for two hours. It was then neutralised, and the reducing sugar estimated. It corresponded with 0.86 gram of dextrose, whereas 2 grams of the amygdalin employed, having the composition $C_{20}H_{27}O_{11}N, 2H_2O$, should yield on complete hydrolysis 1.488 grams of dextrose. On repeating this experiment with a larger amount of material, its rotation in the 1-dm. tube was $\alpha_D + 0.85^\circ$, whereas, had hydrolysis to dextrose and *l*-mandelonitrile glucoside been quantitative, it should have been approximately $+0.7^\circ$. The solution was exactly neutralised with a standard solution of barium hydroxide, and, after the barium sulphate had settled, the clear liquid was decanted and evaporated to a thick syrup in a vacuum. It was then extracted with a small quantity of boiling alcohol, and this solution fractionally precipitated by ethyl acetate. The first crop was obviously impure *l*-mandelonitrile glucoside, as its specific rotation was $[\alpha]_D - 18.1^\circ$, but subsequent crops approximated more closely to the value for that substance, namely, $[\alpha]_D - 26.5^\circ$, and on recrystallisation the correct value was obtained. The results of these experiments show that the biose junction in the molecule of amygdalin is the point most susceptible of attack by sulphuric acid at all concentrations, just as when dilute hydrochloric acid is employed. They demonstrate, however, the striking difference between the comparative facility with which the latter acid decomposes benzaldehydecyanohydrin and the difficulty with which that is accomplished by sulphuric acid. After heating to 80° for two hours with *N*-hydrochloric acid, Caldwell and Courtauld (*loc. cit.*) estimated that the solution contained hydrocyanic acid equivalent to 14 per cent. of the amygdalin employed, whereas in our experiments with dilute sulphuric acid the amount present must have been extremely small, for the odour of oil of bitter almonds could not be detected with certainty.

Hydrolysis by a Concentrated Aqueous Solution of Oxalic Acid.—This acid has only been examined in concentrated solution, and

even thus at a temperature of 98° its action is very slow relatively to that of hydrochloric and sulphuric acids. An aqueous solution, containing 9.45 grams of crystallised oxalic acid and 10 grams of amygdalin in 50 c.c., was heated on the water-bath at 98° for intervals of three, five, and seven hours, and estimations were made of the liberated hydrocyanic acid and reducing sugar. The results were as follows:

Time.	Dextrose.	Hydrocyanic acid.
3	40.0	14.8
5	51.7	24.5
7	59.5	30.0

The results are expressed in percentages of the total amounts which 10 grams of amygdalin could yield. It seems probable from these figures that oxalic acid resembles dilute hydrochloric in its action, producing first *l*-mandelonitrile glucoside, which it subsequently hydrolyses to dextrose, and the decomposition products of mandelonitrile, but the production of *l*-mandelic acid in small amount is not excluded. To test for this, an experiment was performed, using six times the quantity of material, and the heating was continued for four hours longer. It was then thoroughly extracted with ether, and the residue left on evaporation of the ether was converted into the barium salt. After filtration from a considerable quantity of barium oxalate, the filtrate was evaporated to dryness, and the soluble acid again extracted with ether after acidifying with hydrochloric acid. There were thus obtained 1.387 grams melting at 118–126° and showing $[\alpha]_D - 136^\circ$. The corresponding values for pure *l*-mandelic acid are 132° and -154° . It was therefore mainly *l*-mandelic acid contaminated with a little of the racemic acid, which melts at 118°, and the yield was about 8 per cent. of the theoretical. Although Caldwell and Courtauld did not succeed in demonstrating the production of this substance when *N*-hydrochloric acid is employed as hydrolyst, it is not improbable that a small quantity is produced in that case also.

Trichloroacetic Acid.—A solution containing 10 grams of amygdalin, 36 grams of acid, and 25 c.c. of water, having a total volume of 55 c.c., was kept at 18°. It required several hours for total solution. Its rotation in the 1-dcm. tube was $\alpha_D - 8.3^\circ$, and this remained constant for four weeks. The solution is 4*N* with respect to acid, and, as no determinations had been made with a corresponding strength of hydrochloric acid at that temperature, a solution was made up containing 10 grams of amygdalin in 55 c.c., the diluent being 4.4*N*-hydrochloric acid. In contrast to the above, its rotation in the 1-dcm. tube varied in sixteen

days from $\alpha_D - 7.7^\circ$ to -20.05° . The solution containing trichloroacetic acid was then heated for twenty-four hours at 45° , but when cooled and again examined its rotation was found to be unaltered. Thinking that the relatively small quantity of water present in this solution might be responsible for such an anomalous result, we diluted 10 c.c. of it to 20 c.c. The observed angle was now $\alpha_D - 4.15^\circ$, and it remained constant during nineteen days at 18° . Trichloroacetic acid, therefore, does not appear to hydrolyse amygdalin at all under conditions similar to those at which hydrochloric acid effects complete hydrolysis.

The hydrolytic activity of acids is commonly ascribed to the hydrogen ion which they contain, and this property has been employed in a great number of well-known instances as a measure of the relative affinity of the acids. Further, a large number of other methods have been developed for measuring the affinities of acids, and these, although not yielding absolutely concordant results, nevertheless give values for any particular acid which are at least of the same order of magnitude. All of these methods indicate that trichloroacetic acid is not quite, but nearly, as strong as hydrochloric acid. However, as regards their power of hydrolysing amygdalin, we find that the two do not even appear in the same category. The amygdalin molecule is, however, exceptional among the hydrolysts which have been examined, in that it has several points, totally different from each other in their chemical nature, susceptible to the action of the hydrolyst, and it may well be that a similar examination of other substances presenting such features will show parallel behaviour. In a recent investigation, Adrian J. Brown (*Proc. Roy. Soc.*, 1909, B, **81**, 82) has found an instance of selective action on the part of some acids. He has observed that whilst the coverings of the seeds of *Hordeum vulgare* are readily permeable to trichloroacetic acid in aqueous solution, they are quite impermeable to hydrochloric and sulphuric acids.

It would be idle at present to suggest an explanation of this anomaly, but a much more extended investigation will be made embracing many other acids as well as derivatives of amygdalin to discover, if possible, something of the nature of this selective affinity.

MACDONALD CHEMISTRY AND MINING BUILDING,
MCGILL UNIVERSITY.

CLIV.—2 : 3 : 5-Trinitro-4-aminophenol and Derivatives.

By RAPHAEL MELDOLA, F.R.S., and JAMES GORDON HAY, A.I.C.

THE acetyl derivative of the above compound has been fully described in a series of papers published during the last few years (Trans., 1906, 89, 1935; 1907, 91, 1477; 1908, 93, 1659; 1909, 95, 1033), but the corresponding trinitroaminophenol has only been incidentally referred to (*loc. cit.*, 91, 1477). As no trinitro-derivative of para-aminophenol has hitherto been prepared, and as the acetyl derivative has proved to be of especial interest on account of its reactivity, the parent trinitro-compound seemed worthy of detailed study from several points of view. In the first place, with respect to the possibility of catenation products being formed from this compound by interaction with amines in the same way as with the acetyl derivative, it may be pointed out that, as no ring-formation would be possible in this case, the products would be ortho-amino-derivatives of substituted diaryl- or arylalkyl-amines :

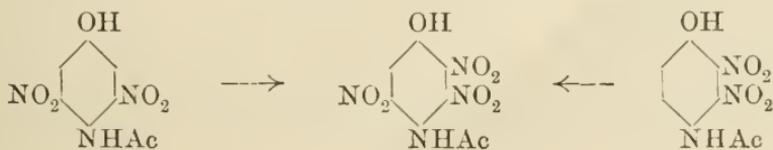


Compounds of this type have hitherto been but little studied on account of the difficulty of preparing them, and it was therefore hoped that the new trinitroaminophenol would prove to be a convenient material for synthesising them according to the above scheme. Our experiments in this direction have, however, so far led to negative results, and no definite compound has been obtained by the interaction of trinitroaminophenol and amines under any conditions. The addition of the amine to the alcoholic solution of the trinitro-compound leads in the first place to the formation of a highly coloured (generally violet) salt, which rapidly decomposes at the ordinary temperature. The trinitro-compound is apparently completely decomposed by amines, with the formation of resinous products. Although the study of these products of decomposition has for the present been abandoned, the research will be continued at some future time, as it is not improbable that by modifying the conditions under which the reaction takes place the required catenation products may be obtained.

The other direction in which the trinitroaminophenol has been studied is its behaviour on diazotisation, as the conditions are apparently most favourable for the elimination of a nitro-group in accordance with the rule which has been found to hold good in the case of the dinitroanisidines. It will be seen in the experimental part of this

paper that the 3-nitro-group in the trinitro-compound is not eliminated on diazotisation, a fact of considerable interest when considered in connexion with the results made known in a former paper (Trans., 1907, 91, 1482). It was shown in this last paper that 2 : 3-dinitro-4-aminophenol does not lose the 3-nitro-group on diazotisation, although the latter is in a favourable ortho-position with respect to the amino-group. From this fact it was concluded that it is the methoxy-group which is the "loosening" substituent in this and analogous cases, since the corresponding dinitroanisidine readily parts with the 3-nitro-group on diazotisation (*loc. cit.*, p. 1484). This conclusion receives confirmation from the fact made known in the present paper that 2 : 3 : 5-trinitro-4-aminophenol also retains the 3-nitro-group on diazotisation, since in this case the amino-group (and therefore the diazonium group) is ortho with respect to two nitro-groups. The corresponding trinitro-*p*-anisidine has not been obtained by us, although attempts have been made to prepare this compound by the direct methylation of the silver salt of the trinitro-acetylaminophenol (Trans., 1906, 89, 1937), and by the extreme nitration of aceto-*p*-anisidide. In the mean time a trinitroanisidine of the required constitution appears to have been obtained in small quantity by Reverdin by the extreme nitration of benzo-*p*-anisidide in acetic anhydride solution (*Arch. Sci. phys. nat.*, 1909, 27, 395).

The process originally described for the preparation of trinitro-acetyl-*p*-aminophenol (Trans., 1906, 89, 1936) has in the course of our work been considerably improved, and we are now enabled to give the details of the method finally adopted. In the earlier process the diacetyl derivative of *p*-aminophenol was nitrated so as to furnish as the first product the mononitro-compound of Hähle, and this by further nitration was converted into the trinitroacetylaminophenol. In a subsequent communication we pointed out that if the mononitro-compound is partially hydrolysed so as to convert it into the 3-nitro-4-acetylaminophenol, and the latter nitrated under regulated conditions, 2 : 3-dinitro-4-acetylaminophenol is formed (Trans., 1907, 91, 1481). In this last paper it was also stated that by extreme nitration the mononitroacetylaminophenol is converted into the 2 : 3 : 5-trinitro-compound. The formation of the latter from 2 : 3-dinitro-4-acetylaminophenol as well as from 3 : 5-dinitro-4-acetylaminophenol (Trans., 1906, 89, 1936) thus furnishes an additional proof of the constitution which we originally assigned to this compound :



From these results it appears, also, that the course of nitration is different, according as the mono- or the di-acetyl derivative of the mononitro-compound is used as the initial stage, although the final product is the same in both cases. The orienting influence of the *O*-acetyl group thus determines the entry of the second nitro-group into position 5, leaving only position 2 (or 6) for the third nitro-group. The hydroxyl group, on the other hand, sends the second nitro-group into position 2, leaving positions 5 and 6 for the third nitro-group, which in fact enters position 5.

EXPERIMENTAL.

Preparation and Properties of Trinitroacetylaminophenol.

3-Nitro-4-acetylaminophenol is prepared by hydrolysing the diacetyl derivative in the way previously described (Trans., 1907, **91**, 1481, footnote). The success of this operation depends on the rapidity with which the hydrolysis is effected, and the use of just sufficient alkali to bring about solution at the ordinary temperature. If an excess of alkali is present, or if the solution when once formed is not immediately acidified, there is much loss of material, owing to the decomposing action of the alkali. The 3-nitroacetyl-amino-compound, after precipitation, is collected, washed with water, dried, and further nitrated by dissolution in fuming nitric acid (D 1.5). One hundred c.c. of acid will nitrate 30 grams of the mononitro-compound, the latter being gradually stirred into the acid kept cool in melting ice. When all the substance has been dissolved in the acid, the solution is at once poured on to ice, and the trinitro-compound collected as soon as it has separated. As this last compound is decomposed on long standing in presence of dilute nitric acid, it is advisable to collect the precipitate and wash it free from acid with as little delay as possible. Owing to the solubility of the trinitro-compound in water, the quantity of ice used for precipitation must also be limited to a minimum, or considerable loss of material is incurred. The best solvent for purifying the crude product is acetic acid, one crystallisation being generally sufficient to give a pure compound if the above method of preparation is followed.

Some of the general properties of 2:3:5-trinitro-4-acetylaminophenol have been described in former papers. The extreme reactivity of the compound renders it unsafe to dry it in contact with organic matter, such as filter paper. If dried in the water-oven on a paper filter, deflagration takes place, although it may be safely dried in contact with glass or porcelain. The extreme readiness with which the 3-nitro-group is eliminated renders it impossible to prepare salts by combining the compound with strong bases, as the latter cause complete decom-

position. Attempts to replace the mobile nitro-group by methoxy- or ethoxy-groups by interaction with sodium methoxide or ethoxide gave only resinous products. The extremely acid character of the compound enables it to decompose metallic salts containing weaker acid radicles, and this property has enabled us to isolate the *potassium* and *sodium* salts. The former was prepared by dissolving the trinitro-compound in a warm solution of potassium cyanide or potassium acetate; the salt separates out on cooling in splendid scarlet needles, which are very soluble in cold water, but which, by rapid washing, can be freed from mother-liquor. The salt was dried at the ordinary temperature in a desiccator, as it deflagrates when heated in the water-oven:

0.0316 gave 0.0082 K_2SO_4 . $K = 11.64$.

$C_8H_5O_8N_4K, H_2O$ requires $K = 11.43$ per cent.

The water of crystallisation could not be determined directly by drying for the reason above stated. The sodium salt was not obtained in sufficient quantity for analysis, as its solubility is greater than that of the potassium salt, and it could not be purified by washing. In appearance it resembles the potassium salt. This method of obtaining salts of the trinitro-compound appears to be generally applicable, and the research is being continued in this direction.

Preparation and Properties of Trinitroaminophenol.

The acetyl derivative cannot be hydrolysed by alkalis, owing to its instability in presence of such reagents. The early attempts to hydrolyse by means of sulphuric acid also failed, as the special properties of the compound were not at the time sufficiently familiar (Trans., 1906, 89, 1937). We have now found that the acetyl group can be completely removed by sulphuric acid and without any decomposition of the trinitroamino-compound if the following method is closely adhered to.

The acetyl derivative is dissolved by stirring in an excess of concentrated sulphuric acid at the ordinary temperature of the laboratory. The vessel containing the solution is then plunged into a bath of boiling water for a few minutes and immediately withdrawn. The course of the hydrolysis must be followed by rapid tests, a drop of the solution being withdrawn on a glass rod at short intervals and diluted with water on a watch-glass. When hydrolysis is complete, a scarlet, crystalline precipitate is formed, and the sulphuric acid solution must be cooled at once by immersion in cold water, or the hydrolysis proceeds too far and decomposition takes place. A brownish tinge shown by the precipitate indicates that the action of the sulphuric acid has been too prolonged, as the pure compound is bright red. The whole operation takes but a few minutes, and its success depends upon arresting the

action of the acid at the critical stage. When the latter point has been reached and the solution cooled, the trinitroamino-compound is precipitated by pouring the solution on to ice. The red, crystalline deposit can be collected and washed with water until free from acid. It cannot be dried at 100° without decomposition. It can be crystallised in small batches from acetic acid, from which it separates in deep red needles having a decomposing point of about 145° :

0.0671 gave 12.65 c.c. N_2 (moist) at 9.5° and 767 mm. $N = 22.84$.

$C_6H_4O_7N_4$ requires $N = 22.96$ per cent.

The compound is but feebly basic, the sulphate being completely dissociated by water. The salts formed with ammonia, alkyl- and aryl-amines, alkaline hydroxides, etc., are of an intense violet colour, but are so unstable that they undergo immediate decomposition.

Diazotisation of the Trinitroaminophenol.

The compound does not diazotise satisfactorily in acetic acid solution, the amino-group being no doubt "protected" by the nitro-groups on either side. In order to effect diazotisation, the substance is dissolved at the ordinary temperature in concentrated sulphuric acid, the solution diluted with a little water, and, when cold, an excess of solid sodium nitrite stirred in in small portions. The course of the diazotisation can be followed by mixing a drop of the solution with water on a watch-glass; the diazonium salt is decomposed by water with the precipitation of a bright yellow diazo-oxide (quinonediazide), so that the appearance of a yellow instead of a red precipitate on dilution indicates the completion of the reaction.

2 : 3 : 5-Trinitrophenol.

The solution of the diazonium sulphate prepared as above undergoes the usual "diazo-decompositions" with various reagents. On boiling with excess of absolute alcohol as long as nitrogen is evolved, evaporating the solvent, and diluting with water, trinitrophenol crystallises out in ochreous needles. This compound, which is of interest as being an isomeride of picric acid, has been briefly referred to in a recent note (*J. Soc. Dyers*, 1909, 25, 12). It is slightly soluble in boiling water, from which it separates in yellow needles, melting at $119-120^{\circ}$, and becoming ochreous and opaque on drying at 100° . It is readily soluble in alcohol, acetic acid, or benzene :

0.0852 gave 13.35 c.c. N_2 (moist) at 17° and 764 mm. $N = 18.24$.

$C_6H_3O_7N_3$ requires $N = 18.34$ per cent.

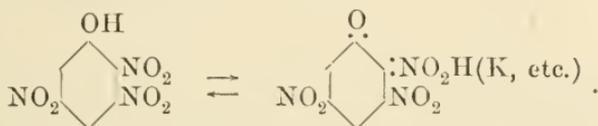
This trinitrophenol dyes silk and wool with a more orange shade than picric acid. The hydroxyl group is so effectively protected that

the compound could not be satisfactorily methylated or acetylated by any of the ordinary methods. On dissolving in hot potassium carbonate solution, a potassium salt separates out on cooling in red needles, which contain no water of crystallisation :

0.1672 gave 0.0554 K_2SO_4 . $K = 14.81$.

$C_6H_2O_7N_3K$ requires $K = 14.66$ per cent.

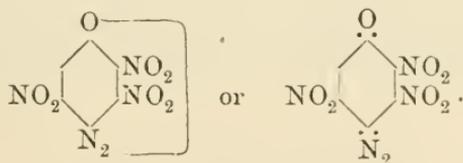
Other salts were prepared and examined qualitatively. When dry, they deflagrate on heating, and are not at all comparable in explosive power with the picrates. The solutions of the trinitrophenol are much more highly coloured than the solid compound, a property which, taken in connexion with the deep red colour of the salts, suggests the usual *isonitro*-tautomerism :



The trinitrophenol appears to form a molecular compound with naphthalene, which crystallises from alcohol in orange needles melting at 100—101°. This compound is, however, much less stable than the corresponding picrate, and the successive analyses following the crystallisations indicated that dissociation takes place in alcoholic solution.

From the foregoing results, it follows that there is no loss of a nitro-group on diazotisation.

2 : 3 : 5-Trinitroquinonediazide,



The diazonium sulphate prepared as described is immediately decomposed on dilution with water, with the formation of a quinone-diazide, which separates as a dense, yellow, micro-crystalline powder. After being washed free from acid, the compound, although highly explosive, can be safely dried in the water-oven. It has been found very difficult to obtain the substance perfectly pure, as it is decomposed by most solvents, and tends to retain those which do not interact with it chemically. The analytical results are, however, perfectly definite in establishing the fact that no loss of a nitro-group occurs on the transformation of the diazonium salt into the quinonediazide. The latter is, in fact, unchanged by a solution of sodium acetate at the ordinary temperature, although complete decomposition with the

formation of resinous products is caused by the action of solutions of alkalis or of alkaline carbonates. The compound can be crystallised from boiling glacial acetic acid, provided the quantity is limited to about half a gram. Boiling with this solvent causes some amount of decomposition, as shown by the evolution of nitrous fumes, but the loss is not serious if the scale of working is not too large. From the hot saturated solution, the compound separates on cooling in dense, ochreous prisms, the decomposing point of which was not determined on account of the highly explosive character of the substance. Analysis indicates that all the nitro-groups are retained :

0.0574 gave 13.05 c.c. N_2 (moist) at 13° and 765 mm. $N = 26.98$.

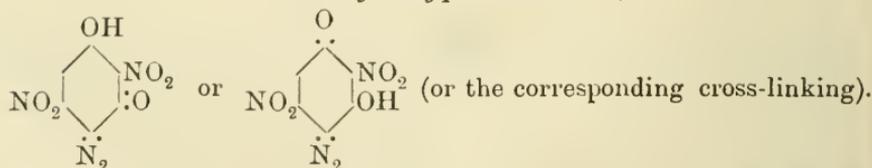
0.0574 ,, 13.23 ,, N_2 ,, ,, 14° ,, 764.3 mm. $N = 27.25$.

$C_6HO_7N_5$ requires $N = 27.45$ per cent.

This quinonediazide couples with β -naphthol with extreme difficulty, a property which is probably due to the protective action of the 3- and 5-nitro-groups on the intermediate diazo-group. In the presence of pyridine or an alkali, an azo-compound is formed, but there is also further decomposition, due to the elimination of one of the nitro-groups, the mobility of which is increased by the proximity of the azo-naphthol complex. The azo-compound thus formed appears to be a mixture of extremely insoluble products, which will require further study before any definite conclusion concerning their nature can be drawn.

The 3-nitro-group in the quinonediazide being in a favourable position for displacement, attempts were made to arrive at definite products by the substitution of other radicles for this group. Boiling with sodium acetate solution or with absolute alcohol brings about definite decomposition, the latter in a quite unexpected way.

Dinitrohydroxyquinonediazide,



The trinitro-compound dissolves in a strong boiling solution of sodium acetate without any considerable evolution of nitrogen, and, on cooling, a dense, orange, crystalline sodium salt separates. The latter was collected, washed, redissolved in a small quantity of hot water, and acidified with hydrochloric acid. Large, golden scales separated on cooling, and these had all the properties of a quinonediazide, being highly explosive and coupling readily with β -naphthol

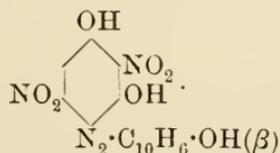
in presence of alkali. From this result it appears that the 3-nitro-group is more readily removed than the diazo-group :

0.0614 gave 13.05 c.c. N_2 (moist) at 18° and 767.1 mm. $N = 24.76$.

$C_6H_2O_6N_4$ requires $N = 24.78$ per cent.

The compound may have either of the above formulæ. Although the ortho-quinonediazide must be the first product resulting from the displacement of the 3-nitro-group, it may easily undergo isomeric transformation into the para-compound if the latter configuration is the more stable. In view of the explosive character of the compound, we are inclined to believe that it possesses the para-constitution, as the ortho-quinonediazides are not, as a rule, so highly explosive. It is, however, impossible at present to decide conclusively between these formulæ.

The quinonediazide in a pasty and moist condition combines with β -naphthol dissolved in sodium hydroxide, giving a highly-coloured and dense, crystalline deposit of a sodium salt having a bronzy lustre. This salt can be collected and washed with a dilute solution of sodium hydroxide until free from excess of naphthol. The azo-compound, liberated by hydrochloric acid from the sodium salt, dissolves very sparingly in boiling glacial acetic acid, from which it separates on cooling in dull red needles, which begin to blacken about 240° , but do not melt at 320° . The azo-compound is phenolic in character, dissolving in aqueous ammonia or very dilute sodium hydroxide with an indigo-blue colour, which changes to red on adding more sodium hydroxide. This colour change most probably indicates the formation of a disodium salt from a mono-sodium salt, as there are two hydroxyl groups in the molecule, and it seems unnecessary in such a case to introduce any hypothesis of structural change on the chemical evidence only. From its mode of formation, the compound must be an azo-naphthol derivative of 2 : 5-dinitroresorcinol :



0.070 gave 8.95 c.c. N_2 (moist) at 13° and 759.7 mm. $N = 15.1$.

$C_{16}H_{10}O_7N_4$ requires $N = 15.14$ per cent.

Concentrated sulphuric acid dissolves the compound with a reddish-violet colour, which becomes redder, and finally gives an orange, gelatinous precipitate on dilution with water. It is probable that this same azo-compound is among the products of the action of the trinitroquinonediazide on β -naphthol in presence of alkali.

The decomposition of the trinitroquinonediazide by boiling absolute alcohol leads to the formation of a compound the analysis of which

indicates that a nitro-group is replaced by the ethoxy-group. The study of this reaction is being continued.

The cost of this research has been partly met by a grant from the Government Grant Fund of the Royal Society, a source of assistance which we have much pleasure in acknowledging.

FINSBURY TECHNICAL COLLEGE.

CLV.—*The Partial Racemism of Menthyl r -Mandelate.*

By ALEXANDER FINDLAY and EVELYN MARION HICKMANS, M.Sc.

IT has already been shown (Trans., 1907, 91, 905) from a study of the freezing-point curves of the *l*-menthyl ester of the mandelic acids that *l*-menthyl *r*-mandelate exists as a definite compound with the melting point 83.7°. It was of importance, therefore, to investigate the stability of the compound at lower temperatures, in order to ascertain whether the transition point below which the partial racemate would be unstable is sufficiently accessible to allow of the resolution of *r*-mandelic acid by crystallisation of the *l*-menthyl ester.

The experiments of A. McKenzie (Trans., 1904, 85, 1255) indicated that the partial racemate is stable also at the ordinary temperature, but nothing was known as to how far the transition point might lie below this. For the investigation of this point, experiments based on fractional crystallisation, although frequently employed in other cases, are very unsuitable, owing to the possible occurrence of supersaturation, difference in velocity of crystallisation, etc. These factors may complicate, and apparently in some cases have complicated, the problem and led to false conclusions.*

* In this connexion, reference may be made to a paper recently published by Professor Kipping (Trans., 1909, 95, 408), in which he points out that whereas, for example, *d*-hydrindamine *r*-mandelate can be resolved by crystallisation from aqueous solution, the *dl*-hydrindamine *d*-mandelate could not be so resolved. This behaviour is considered as indicating the existence of partially racemic molecules in solution. Although the writer is also of opinion that racemic and partially racemic molecules can exist in the liquid state and in solution (compare *Trans. Faraday Soc.*, 1907, 3, Part 2), he does not consider that this is of particular importance for the question of the resolution of a racemic compound by crystallisation. What is of importance is not what compounds exist in solution, but what solid substances can exist in equilibrium with the solution. Although, no doubt, the substances *dA₁B* and *lAdB* (in the nomenclature of Professor Kipping) have the same solubility, the partially racemic compounds *dA₁B*+*dAdB* and *dAdB*+*lAdB* are two distinct compounds with their own solubility and stability conditions, including transition

The determination of solubility with the partially racemic material alone as solid phase, and again with the partially racemic material along with one of the optical antipodes as solid phases (equilibrators), gives a simple and sure method of attacking the problem (Roozeboom, *Zeitsch. physikal. Chem.*, 1899, **28**, 494). In this way one learns the conditions under which the partial racemate is stable, and resolution into the optical antipodes therefore impossible; and the conditions under which the resolution can be effected.

Solubility determinations have been carried out by Ladenburg and Doctor in the case of the strychnine tartrates (*Ber.*, 1899, **32**, 50), whereby they showed that strychnine *r*-tartrate exhibits a transition point at 30°, below which it is stable, but above which it breaks up into the strychnine salts of the optically active forms. Resolution therefore is possible only at temperatures above the transition point.

Similarly, *r*-tetrahydroquinidine hydrogen tartrate exhibits a transition point at 59°, and is stable above that temperature (Ladenburg and Herrmann, *Ber.*, 1908, **41**, 966. A summary of the work on partial racemism is given in *Annalen*, 1909, **364**, 227).

The method pursued by Ladenburg and Doctor in the former of the two cases mentioned was to determine the solubility curves of strychnine *r*-tartrate, strychnine *d*-tartrate, and strychnine *l*-tartrate separately, the transition point being indicated by a break in the curve. The picture of the relationships obtained in this way is, however, incomplete, and it is better to determine a series of isothermal solubility curves with, in the first place, the partial racemate, and each of the optical antipodes as single solid phases; and, in the second place, with the racemate together with each of the optical antipodes separately as solid phases. This method of investigation has been of the greatest value in the case of ordinary double salts, and it is the method which we have employed in the case of the menthyl mandelates. The results obtained are all the more of interest on account of the fact that they constitute the first experimental values of the kind for partially racemic substances.

temperature. Although, therefore, the former partial racemate may be unstable under the conditions of crystallisation employed by Professor Kipping, it does not follow that the latter partial racemate should also be so. Resolution, therefore, might be effected in the former but not in the latter case. Such resolution, however, would no doubt be effected by crystallisation at a suitable temperature, at which the latter partial racemate is also unstable. The temperature above or below which this instability occurs (the transition temperature) can, of course, be determined only by experiment, and it is greatly to be desired that this be done, most simply by the solubility method, as described in the present paper. The method of fractional crystallisation, even when the temperature is regulated, is not so suitable, and gives much less information. The temperature conditions, moreover, do not appear to have received sufficient consideration by Professor Kipping.—A. F.

EXPERIMENTAL.

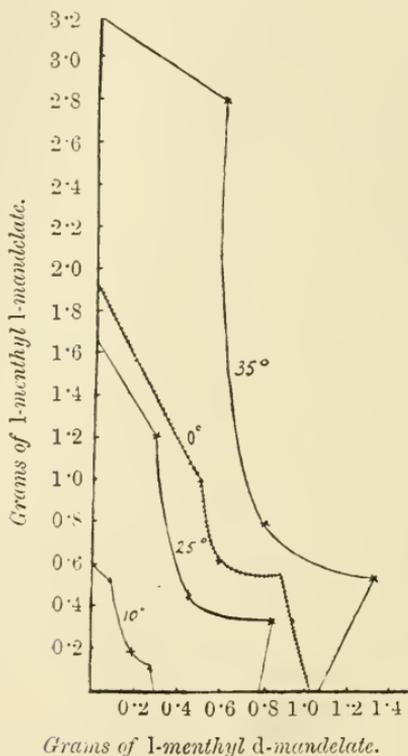
The esters employed were prepared as described in our previous paper (*loc. cit.*). The specific rotations of the esters in alcoholic solution were :

l-Menthyl *d*-mandelate, $[\alpha]_D^{17.5} - 9.45^\circ$.

l-Menthyl *l*-mandelate, $[\alpha]_D^{20} - 140.92^\circ$.

l-Menthyl *r*-mandelate, $[\alpha]_D^{11.3} - 75.03^\circ$.

The solubility was determined by shaking a quantity of the solvent with excess of the particular solid or solids until saturation occurred.



A certain quantity of the solution was removed by means of a pipette furnished with a small filter, and weighed. It was then evaporated to dryness on the water-bath, and the total amount of dissolved ester thus obtained. Where one was not dealing with a single substance, the composition of the solution expressed in terms of the menthyl ester of the *d*- and *l*-antipodes was determined polarimetrically.

In the case of the solubility determinations at 0° , however, the solution was prepared at the ordinary temperature, placed along with

a quantity of the appropriate solid in melting ice, and shaken frequently. These experiments were repeated several times until concordant values were obtained.

The determinations were carried out at the temperatures 35°, 25°, and 10°, using 80 per cent. alcohol (by volume: $d_4^{25^\circ} = 0.8517$) as solvent, and at 0°, using absolute alcohol as solvent. The results obtained are summarised in the following tables, and are represented graphically in the figure.

In the following tables, *D* represents *l*-menthyl *d*-mandelate; *L*, *l*-menthyl *l*-mandelate; and *R*, *l*-menthyl *r*-mandelate. In almost all cases the values are the mean of two sufficiently concordant determinations.

Solubilities at 35°.

Solid phases.	<i>D.</i>	<i>L.</i>	<i>R.</i>	<i>D+R.</i>	<i>L+R.</i>
Total solid (in grams) in 10 grams of solvent	1.03	3.19	1.60	1.89	3.43
Weight of <i>L</i> in 10 grams of solvent ..	—	3.19	0.80	0.544	2.83
Weight of <i>D</i> in 10 grams of solvent	1.03	—	0.80	1.350	0.60

Solubilities at 25°.

Solid phases.	<i>D.</i>	<i>L.</i>	<i>R.</i>	<i>D+R.</i>	<i>L+R.</i>
Total solid (in grams) in 10 grams of solvent	0.595	1.64	0.896	1.203	1.458
Weight of <i>L</i> in 10 grams of solvent	—	1.64	0.448	0.321	1.192
Weight of <i>R</i> in 10 grams of solvent	0.595	—	0.448	0.882	0.267

Solubilities at 10°.

Solid phases.	<i>D.</i>	<i>L.</i>	<i>R.</i>	<i>D+R.</i>	<i>L+R.</i>
Total solid (in grams) in 10 grams of solvent	0.287	0.595	0.369	0.404	0.593
Weight of <i>L</i> in 10 grams of solvent	—	0.595	0.184	0.113	0.505
Weight of <i>D</i> in 10 grams of solvent	0.287	—	0.184	0.291	0.088

Solubilities at 0° (in absolute alcohol).

Solid phases.	<i>D.</i>	<i>L.</i>	<i>R.</i>	<i>D+R.</i>	<i>L+R.</i>
Total solid (in grams) in 10 grams of solvent	1.06	1.93	1.25	1.45	1.57
Weight of <i>L</i> in 10 grams of solvent	—	1.93	0.625	0.535	1.03
Weight of <i>D</i> in 10 grams of solvent	1.06	—	0.625	0.915	0.54

I. *Solubilities at 35°.*A. Solid phase: *L*.

- (1). Solution, 6.7599; ester, 1.6031.
 (2). ,, 4.1783; ,, 1.0085.

B. Solid phase: *D*.

Solution, 8.3763; ester 0.8183

C. Solid phase: *R*.

- (1). Solution, 8.5414; ester, 1.1675.
 (2). ,, 8.4720; ,, 1.1842.

D. Solid phases: *L + R*.

- (1). Solution, 8.7408; ester, 2.2449.
 (2). ,, 8.7500; ,, 2.2265.

Rotation: (1). $c = 2.6995$. $\alpha_D^{14.6} - 6.32^\circ$, $[\alpha]_D^{14.6} - 117.06^\circ$
 (2). $c = 3.0105$. $\alpha_D^{14.3} - 7.14^\circ$, $[\alpha]_D^{14.3} - 118.76$

E. Solid phases: *D + R*.

- (1). Solution, 8.4957; ester, 1.3319.
 (2). ,, 8.5680; ,, 1.3840.

Rotation: (1). $c = 3.9555$. $\alpha_D^{14} - 3.74^\circ$, $[\alpha]_D^{14} - 47.27^\circ$.
 (2). $c = 4.0385$. $\alpha_D^{14} - 3.81^\circ$, $[\alpha]_D^{14} - 47.17^\circ$.

II. *Solubilities at 25°.*A. Solid phase: *L*.

- (1). Solution, 8.5947; ester, 1.2219.
 (2). ,, 8.7410; ,, 1.2182.

B. Solid phase: *D*.

- (1). Solution, 8.5006; ester, 0.4739.
 (2). ,, 8.4645; ,, 0.4799.

C. Solid phase: *R*.

- (1). Solution, 8.5344; ester, 0.6997.
 (2). ,, 8.5908; ,, 0.7163.

D. Solid phases: *L + R*.

- (1). Solution, 8.5757; ester, 1.0865.
 (2). ,, 7.8732; ,, 1.0068.

Rotation: (1). $c = 2.8095$. $\alpha_D^{14} - 6.45^\circ$, $[\alpha]_D^{14} - 114.80^\circ$.
 (2). $c = 2.1055$. $\alpha_D^{14.5} - 5.01^\circ$, $[\alpha]_D^{14.5} - 118.9^\circ$.

E. Solid phases: *D + R*.

Solution, 8.5476; ester, 0.9181.

Rotation: $c = 2.7435$. $\alpha_D^{15} - 2.45^\circ$, $[\alpha]_D^{15} - 44.65^\circ$.

III. *Solubilities at 10°.*A. Solid phase : *L*.

- (1). Solution, 8·5887 ; ester, 0·4802.
 (2). „ 8·5310 ; „ 0·4807.

B. Solid phase : *D*.

- (1). Solution, 8·5732 ; ester, 0·2404.
 (2). „ 8·5878 ; „ 0·2396.

C. Solid phase : *R*.

- (1). Solution, 8·4464 ; ester, 0·2960.
 (2). „ 8·5750 ; „ 0·3102.

D. Solid phases : *L + R*.

- (1). Solution, 8·6417 ; ester, 0·4781.
 (2). „ 8·4306 ; „ 0·4774.

- Rotation : (1). $c = 2·2585$. $\alpha_D^{14.5} - 5·50^\circ$, $[\alpha]_D^{14.5} - 121·76^\circ$.
 (2). $c = 2·2185$. $\alpha_D^{13.6} - 5·36^\circ$, $[\alpha]_D^{13.6} - 120·8^\circ$.

E. Solid phases : *D + R*.

- (1). Solution, 8·6024 ; ester, 0·3300.
 (2). „ 8·5986 ; „ 0·3374.

- Rotation : (1). $c = 1·5995$. $\alpha_D^{20} - 1·50^\circ$, $[\alpha]_D^{20} - 46·88^\circ$.
 (2). $c = 1·6300$. $\alpha_D^{14} - 1·45^\circ$, $[\alpha]_D^{14} - 44·49^\circ$.

IV. *Solubilities at 0°.*A. Solid phase : *L*.

- (1). Solution, 7·2929 ; ester, 1·1961.
 (2). „ 8·1149 ; „ 1·2956.

B. Solid phase : *D*.

- (1). Solution, 5·4192 ; ester, 0·5144.
 (2). „ 4·7118 ; „ 0·4622.

C. Solid phase : *R*.

- (1). Solution, 7·2976 ; ester, 0·8273.
 (2). „ 4·6545 ; „ 0·5072.

D. Solid phases : *L + R*.

- (1). Solution, 8·1281 ; ester, 0·0701.
 (2). „ 6·3897 ; „ 0·8927.

- Rotation : (1). $c = 3·2315$. $\alpha_D^{14} - 6·14^\circ$, $[\alpha]_D^{14} - 95·00^\circ$.
 (2). $c = 4·4025$. $\alpha_D^{14.5} - 8·53^\circ$, $[\alpha]_D^{14.5} - 96·87^\circ$.

E. Solid phases : *D + R*.

- (1). Solution, 4·9148 ; ester, 0·6735.
 (2). „ 7·9437 ; „ 0·9271.

- Rotation : (1). $c = 3·2825$. $\alpha_D^{14} - 3·79^\circ$, $[\alpha]_D^{14} - 57·73^\circ$.
 (2). $c = 3·4015$. $\alpha_D^{14.2} - 3·95^\circ$, $[\alpha]_D^{14.2} - 58·06^\circ$.

On examining the solubility isothermals as shown in the figure, it will be seen that each isothermal consists of three parts, the inter-

mediate curve representing the composition of solutions in equilibrium with the partial racemate as solid phase. The existence of this intermediate curve therefore indicates that at all temperatures down to 0° the partial racemate is stable. It will therefore not be possible at temperatures above 0° to resolve *r*-mandelic acid by simple crystallisation of its *l*-menthyl ester.

Crystallisation Experiments.—As the determination of solubility at temperatures below 0° is troublesome, we have sought to ascertain whether the transition point was nearly attained by carrying out a crystallisation experiment at about -15° . A solution of the partially racemic ester in absolute alcohol was prepared at the ordinary temperature, and placed in a bath at about -15° . After crystallisation of part of the dissolved solid had occurred, the mother liquor was drawn off, and the separated crystals were examined under the microscope. Only needle-shaped crystals were observed, and these were found to have a rotation $[\alpha]_D^{15} - 76.4^{\circ}$ (*l*-menthyl *r*-mandelate has $[\alpha]_D^{13.3} - 75.03^{\circ}$). If resolution had taken place, it was to be presumed that the less soluble *l*-menthyl *d*-mandelate would have separated out, and the mother liquor would therefore be relatively rich in *l*-menthyl *l*-mandelate. This apparently was not the case, for on evaporating the mother liquor to dryness and then determining the activity of the residue, the values found were $[\alpha]_D^{13.5} - 74.11^{\circ}$, $[\alpha]_D^{15} - 70.4^{\circ}$, and $[\alpha]_D^{16} - 71.41^{\circ}$. It appears therefore probable that even down to a temperature of -15° the partial racemate is still stable, and resolution by crystallisation therefore impossible.

CHEMICAL DEPARTMENT,
UNIVERSITY OF BIRMINGHAM.

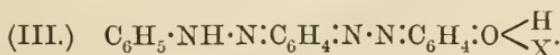
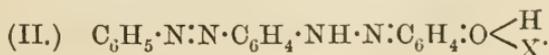
CLVI.—*The Colour and Constitution of Azo-Compounds.*
Part IV.

By JOHN THEODORE HEWITT and FERDINAND BERNARD THOLE.

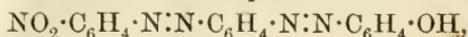
IN the development of the industry of the azo-dyestuffs it has been recognised for many years that an increased depth of tone, accompanied by a shifting of absorption towards the red end of the spectrum, can in many cases be conveniently effected by the substitution of constituents containing a naphthalene nucleus for those of simple benzenoid type, whilst a further change in the same direction may be attained by increasing the number of azo-groups, provided that these are arranged in a suitable manner. The present paper is concerned with the second of these problems, and only benzenoid compounds have been dealt with, but isomeric compounds of mixed type in which naphthalene and benzene nuclei are both present, but their positions in the chain have been interchanged, are under examination, and it is hoped that the results obtained will be shortly ready for publication.

One of the authors of the present communication, in conjunction with H. V. Mitchell (*Trans.*, 1907, **91**, 1251) and J. J. Fox (*ibid.*, 1908, **93**, 333), has already drawn attention to the manner in which a decrease in the principal vibration frequency of an azo-compound accompanies an increase in the length of chain of conjugated double linkings, and it appeared not at all improbable that in the case of non-sulphonated polyazo-compounds containing hydroxyl or alkylated amino-groups as "auxochromes," considerable light might be thrown on the connexion between the increased length of chain of azo-groups and aromatic nuclei by a study of the substances themselves and their salts with mineral acids.

A point arises as to the extent to which quinonoid structure is set up on salt formation, for it is evident from a consideration of the formulæ that in the case of substances like benzeneazobenzeneazophenol, the quinonoid configuration may confine itself either to the phenolic nucleus when a salt is formed by addition of a mineral acid (Formula II), or may extend further so as to embrace the second nucleus (Formula III):



Should the effect of salt formation be to produce a salt of type III, it might be expected that treatment of the solution of benzeneazobenzeneazophenol in concentrated sulphuric acid with nitric acid would lead to production of a nitrated compound of the formula

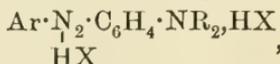


whilst if the quinonoid structure only extended as far as the first benzene nucleus, either the middle benzene nucleus should undergo substitution, or possibly, owing to the para-position being already occupied, no definite result would be obtained. On carrying out experiments on the lines indicated, no satisfactory product of nitration could be isolated, so that one hesitates to draw any definite conclusion.

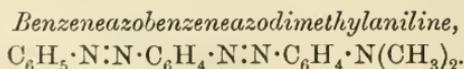
Briefly, however, benzeneazobenzeneazodimethylaniline, itself a compound crystallising in purplish leaflets, and giving orange solutions in neutral solvents, yields a monohydrochloride the hydrochloric acid solution of which is of an intense blue colour. With concentrated sulphuric acid, a red solution is obtained, the substance evidently behaving as a polyacid base, for on adding water the blue colour is produced, whilst further dilution gives rise to an orange shade. That the latter is due to hydrolytic dissociation is evident, addition of ammonia producing no further colour change. The substance thus appears to be a weaker base than dimethylaminoazobenzene, the salts of which are stable with a relatively greater dilution of the acid.

The solution of the corresponding benzeneazobenzeneazophenol in concentrated sulphuric acid is purple; possibly in this case only a monacid salt is formed, for, as will be seen later, the basic properties of this substance are very weak.

The polyacid salts of azo-compounds have already engaged the attention of A. Korczyński (*Ber.*, 1908, **41**, 4379), whilst more recently Hantzsch (*ibid.*, 1909, **42**, 2131) has drawn particular attention to the colour changes accompanying the conversion of benzeneazodimethylaniline into its mono- and di-acid salts. To compounds of the latter type Hantzsch assigns the general formula



on account of the similarity of their absorption spectra to that of solutions of azobenzene in concentrated mineral acids.



To prepare this substance, 9.8 grams of finely powdered aminoazobenzene were mixed with 70 c.c. water and 19.5 c.c. concentrated

hydrochloric acid, a suspension of the hydrochloride being thereby obtained. Under addition of crushed ice and external cooling diazotisation was effected with 3.6 grams sodium nitrite in 20 c.c. water, and the solution filtered into 6 grams of dimethylaniline dissolved in 25 c.c. glacial acetic acid to which a little crushed ice had been added. The excess of mineral acid was removed by adding 5 grams of crystallised sodium acetate, and after three hours the precipitate was collected. Crystallisation from pyridine furnished small purple crystals, melting constantly at 190° (uncorr.):

0.1214 gave 0.3241 CO_2 and 0.0640 H_2O . C = 72.8; H = 5.9.

0.0638 ,, 11.5 c.c. N_2 at 20° and 763 mm. N = 21.2.

$\text{C}_{20}\text{H}_{19}\text{N}_5$ requires C = 72.9; H = 5.8; N = 21.3 per cent.

Hydrochloride, $\text{C}_{20}\text{H}_{19}\text{N}_5\text{HCl}$.—As previously mentioned, the base dissolves in concentrated sulphuric acid with a red colour which passes into blue on dilution, whilst with the most concentrated hydrochloric acid only blue solutions were obtained. In the latter, the head of the band in the visible part of the spectrum corresponds with an oscillation frequency of about 1760. The red sulphuric acid solution evidently corresponds with the orange "azo-salt" of Hantzsch (*loc. cit.*) in the case of dimethylaminoazobenzene, so that it would appear that whilst the latter compound is sufficiently basic to give a di-acid "azo-salt" with concentrated hydrochloric acid, the introduction of a benzeneazo-group in place of hydrogen has considerably weakened the basic properties. The isolation and analysis of the hydrochloride being eminently desirable, 0.5 gram of the substance was boiled with 20 c.c. of alcohol and 5 c.c. of hydrochloric acid, the solution filtered, and slowly concentrated in a desiccator containing sulphuric acid. The resulting crystals showed a fine metallic reflex:

0.1553 gave 0.0599 AgCl. Cl = 9.5.

$\text{C}_{20}\text{H}_{20}\text{N}_5\text{Cl}$ requires Cl = 9.4 per cent. •

The salt gradually loses hydrogen chloride on keeping and falls to a brown powder; this behaviour is to be expected when one considers the ease with which the salt is hydrolysed in aqueous solution.

An attempt to make a dibrominated derivative starting with the dibromoaminoazobenzene ($\text{C}_6\text{H}_5\text{N}_2$: Br : NH_2 : Br = 1 : 3 : 4 : 5) melting at 168° (Berju, *Ber.*, 1884, 17, 1403; Hewitt and Walker, *Trans.*, 1907, 91, 1138) failed, owing to inability to diazotise the amine, even when treated in alcoholic suspension with concentrated sulphuric acid and amyl nitrite and kept overnight. This observation is thought to be worthy of record, since 2 : 4 : 6-tribromoaniline, although difficult to diazotise, is attacked by nitrous acid. Although the hope of examining such a negatively substituted derivative had to be abandoned, a higher homologue has been prepared.

o-Tolueneazo-*o*-tolueneazodimethylaniline,
 $C_6H_4Me \cdot N : N \cdot C_6H_3Me \cdot N : N \cdot C_6H_4 \cdot NMe_2$.

This substance was prepared from the aminoazotoluene described by Nietzki (*Ber.*, 1877, 10, 662). Instead of preparing it by the original method of leading nitrous fumes into *o*-toluidine, a process was adopted analogous to that usually employed in the preparation of aminoazobenzene, and the substance was obtained with constant melting point without recrystallisation. The diazotisation of the aminoazo-compound and coupling with dimethylaniline was effected in the same manner as described for the lower homologue, except that a large bulk of water has to be used for the solution of the tolueneazotolyldiazonium salt. The resulting dimethylamino-compound was crystallised from benzene; it melts at 138° (uncorr.):

0.1329 gave 0.3584 CO₂ and 0.0806 H₂O. C = 74.1; H = 6.6.

0.1204 „ 20.0 c.c. N₂ at 17° and 766 mm. N = 19.8.

C₂₂H₂₃N₅ requires C = 73.95; H = 6.44; N = 19.61 per cent.

The solutions in sulphuric and hydrochloric acids show exactly the same behaviour as those of the lower homologue.

Hydrochloride, C₂₂H₂₃N₅,HCl.—This salt was prepared in the same way as used for benzeneazobenzeneazodimethylaniline hydrochloride:

0.1916 gave 0.0669 AgCl. Cl = 8.6.

C₂₂H₂₃N₅,HCl requires Cl = 9.0 per cent.

Benzeneazobenzeneazophenol, C₆H₅ · N : N · C₆H₄ · N : N · C₆H₄ · OH.—This compound, which has already been prepared by Caro and Schraube (*Ber.*, 1877, 10, 2230), was obtained in the usual manner from diazotised aminoazobenzene and phenol:

0.1328 gave 20.2 c.c. N₂ at 16° and 776 mm. N = 18.4.

C₁₈H₁₄ON₄ requires N = 18.5 per cent.

The azophenol dissolves in concentrated sulphuric acid with a purple colour; the head of the absorption band in the visible spectrum of such a solution corresponds with an oscillation frequency of about 1860; the sulphate has not been isolated. The solubility in concentrated hydrochloric acid is very slight and the solution has an orange tint, so that it is possible that the salt may be largely hydrolysed even in presence of large quantities of the acid.

Unfortunately the monohydrochloride could not be prepared by the usual method of passing hydrogen chloride into a benzene solution of the azophenol, since the latter is nearly insoluble in the cold hydrocarbon. Hydrogen chloride was, therefore, led for several hours over a paste of the azophenol with glacial acetic acid; the mass was then transferred to porous earthenware and dried in an atmosphere of hydrogen

chloride. The freshly prepared salt seems to have been formed by absorption of two molecules of acid (compare Korczyński, *loc. cit.*):

0.1522 gave 0.1085 $\Delta_g\text{Cl}$. $\text{Cl} = 17.62$.

$\text{C}_{18}\text{H}_{14}\text{ON}_4 \cdot 2\text{HCl}$ requires $\text{Cl} = 18.88$ per cent.

$\text{C}_{18}\text{H}_{14}\text{ON}_4 \cdot \text{HCl}$,, $\text{Cl} = 10.52$,,

Hydrogen chloride is gradually lost on standing, salt which had been kept for four days in a corked specimen tube containing only 14.33 per cent. of chlorine. It is evident that the second molecule is rather loosely combined.

Acetyl Derivative.

Two grams of the azophenol were boiled for three hours with 30 grams of acetic anhydride. The solution was poured into hot dilute alcohol and the precipitated acetyl derivative crystallised from glacial acetic acid. Both before and after the latter operation, the same melting point, 178° (uncorr.), was observed:

0.1433 gave 19.1 c.c. N_2 at 15° and 775 mm. $\text{N} = 16.2$.

$\text{C}_{20}\text{H}_{16}\text{O}_2\text{N}_4$ requires $\text{N} = 16.3$ per cent.

EAST LONDON COLLEGE.

CLVII.—*The Quantitative Decomposition of the Anilides: a Study in Steric Influence.*

By OLIVER CHARLES MINTY DAVIS.

THE investigation here described was undertaken with the primary object of measuring the quantitative effect of the orientation of a compound on its chemical reactivity, and incidentally to notice the influence of various substituent groups and elements on this reactivity. There are at least three ways in which stereo-configuration may influence a chemical reaction:

(1) When no side-reaction takes place the effect is to bring about differences in the rate of reaction; in very extreme cases no appreciable quantity of end product would be obtained within a reasonable time, and such a slow reaction would be regarded for practical purposes as not occurring at all.

(2) When side-reactions are possible and the original main reaction is very much retarded, obviously the chief end products would be those due to one or more of these side-reactions. The quickest of the possible reactions would in all cases be the one securing the most of the initial substance, and thus producing the predominant end product.

These original side-reactions might thus be unaltered, or even favoured by the new stereo-configuration, and so the practical result would be the formation of new end products.

(3) There is another possible way in which stereo-configuration might exert an important influence essentially distinct from mere retardation or acceleration of rate of reaction. This is the effect on the chemical affinity of the substance. Little or no work has been done in this field, for it is evident that measurements of rates of reaction afford no satisfactory evidence in regard to affinity relationship.

The only methods of investigating this effect on the chemical affinity is the determination of the position of equilibrium, or the measurement of the corresponding electromotive force.

The present paper contains the results of the kinetic measurements of the anilides in the presence of a small excess of alkali. Here it was found that the decomposition was practically quantitative. Further work is being carried out in acid systems to determine the static equilibria.

EXPERIMENTAL.

The majority of the compounds used could not be obtained commercially, and it was necessary to prepare and purify them.

The nitro-compounds were recrystallised from alcohol, but in the other cases water proved the most suitable solvent; the only liquid member is formo-*m*-toluidide, which was obtained in a state of purity by distillation in a vacuum.

The following analytical data were obtained for those compounds which had not been previously prepared.

m-Chloroformanilide, m. p. 57—58°.

0.2650 gave 22.0 c.c. N₂ (moist) at 21° and 740 mm. N = 9.2.

C₇H₆ONCl requires N = 9.0 per cent.

m-Chloropropionanilide, m. p. 88—89°.

0.2940 gave 20.0 c.c. N₂ (moist) at 19° and 756 mm. N = 7.8.

C₉H₁₀ONCl requires N = 7.6 per cent.

n-Butyro-*o*-toluidide, m. p. 79—80°.

0.233 gave 16.00 c.c. N₂ (moist) at 15° and 762 mm. N = 8.0.

C₁₁H₁₅ON requires N = 7.9 per cent.

n-Butyro-*p*-toluidide, m. p. 74—75°.

0.255 gave 18.00 c.c. N₂ (moist) at 16° and 761 mm. N = 8.2.

C₁₁H₁₅ON requires N = 7.9 per cent.

Method of Experiment.

It was impossible to carry out the experiments at a low temperature on account of the slight solubility of many of the members of the series under examination. The following method was found to give the most concordant results when several control experiments were carried out; hence it was adopted throughout.

A definite weight of the anilide (1/400th gram molecule) was carefully washed into a Jena-glass flask with 50 c.c. of distilled water.* Twenty-five c.c. of *N*/5-sodium hydroxide, free from carbonate, were then added, and the flask fitted with a reflux condenser, the inner tube of which was of Jena glass. The flask was then boiled over wire gauze and a Bunsen flame. At the end of definite periods the boiling was stopped, and the whole contents of the flask titrated with *N*/10-sulphuric acid, using phenolphthalein as indicator.

It was found necessary to make a correction for alkali dissolved from the flasks by the boiling solutions. By allowing 0.1 c.c. of *N*/10-alkali for each hour's boiling, this source of error is reduced to a minimum. To avoid it entirely, for those experiments involving prolonged boiling, a flask made of fine silver was used; the condenser was also provided with a tube containing solid potassium hydroxide, to prevent access of carbon dioxide.

Formula used to express Rate of Hydrolysis.

The results of the experiments demonstrated that the velocity of the reaction is proportional to the concentration of the free alkali, as well as to that of the undecomposed anilide present. Hence *K* is calculated according to the bimolecular formula:

$$K = \frac{1}{t(b-a)} \log. \frac{a}{b} \frac{(b-x)}{(a-x)},$$

in which the time *t* is expressed in hours; all concentrations are expressed in gram-molecules per litre, and Napierian logarithms are employed. The original concentration of the anilide is *a*, and that of the alkali, *b* (always made twice as great).

x is the amount of anilide which has been decomposed up to any given time *t*.

This formula does not strictly apply unless all the anilide is present in solution from the commencement of the reaction. In all cases not specially mentioned in the tables several minutes only were required for complete solution.

* In experiments of short duration, the solution was raised to boiling point before adding the standard alkali. Unless otherwise stated, the solution of anilide was rapid and complete.

Initial incomplete solution would tend to lower the value of the earlier constants in each series, but would not so seriously affect the later ones.

In the few cases in which a fraction of the anilide remained undissolved throughout the duration of the experiment, the results were, nevertheless, calculated according to the same formula.

General Conclusions.

Influence of the Methyl Group.—The stability of the anilides increases with progressive introduction of methyl groups into the acidic group, and is greater when the anilide is derived from an "iso" acid.

This is well shown in the following table :

Compound.	Number of measurements.	Time for 50 per cent. decomposition, in hours.	<i>K</i> (average).
*Formanilide	6	0.14	87.1
*Acetanilide.....	11	3.79	3.20
Propionanilide	12	6.3	1.93
<i>n</i> -Butyranilide	10	13.0	0.934
<i>iso</i> Butyranilide	7	30.7	0.395
<i>n</i> -Valeranilide	3	18.5	0.656
<i>iso</i> Valeranilide	5	92.7	0.131

* Throughout the tables, an asterisk is placed against the names of all the anilides the decomposition of which was actually followed up to more than 98 per cent. The time for 50 per cent. decomposition is calculated from the constant.

In the case of the valerianilides solution was incomplete throughout ; hence only a few experiments were performed.

Only two cases were examined in which the "imidic" hydrogen was replaced by alkyl groups. Methylacetanilide is less resistant to alkalis than acetanilide, whereas ethylacetanilide is far more resistant. The greater instability of methylacetanilide is probably due to the fact that it is the first member of a series, and hence apt to behave anomalously.

Compound.	Number of measurements.	Time for 50 per cent. decomposition, in hours.	<i>K</i> (average).
*Acetanilide.....	11	3.79	3.20
*Methylacetanilide.....	10	3.16	3.84
Ethylacetanilide	10	13.00	0.94

The effect of the methyl group when introduced into the benzene nucleus may be very great, or almost negligible, according to the position it occupies. In all cases where the ortho-position is concerned, the result is a very great diminution in the velocity of hydrolysis.

The influence of the meta- and para-substituents is much less noticeable, and is greatest in the case of the formotoluidides (where, owing to short duration of experiments the errors are apt to be large), and in those compounds where complete solution was not obtained throughout the experiments.

Compound.	Number of measurements.	Time for decomposition, in hours.	<i>K</i> (average).
*Formanilide	6	0·14	87·1
*Formo- <i>o</i> -toluidide	8	0·36	33·9
*Formo- <i>m</i> -toluidide	4	0·16	74·6
*Formo- <i>p</i> -toluidide	4	0·14	82·9
*Acetanilide	11	3·79	3·20
Aceto- <i>o</i> -toluidide.....	11	17·16	0·709
*Aceto- <i>m</i> -toluidide	6	3·89	3·14
*Aceto- <i>p</i> -toluidide	7	3·90	3·11
Propionanilide.....	12	6·29	1·93
Propio- <i>o</i> -toluidide	8	30·36	0·400
Propio- <i>m</i> -toluidide	7	6·42	1·89
Propio- <i>p</i> -toluidide	7	6·57	1·85
<i>n</i> -Butyranilide.....	10	13·02	0·934
<i>n</i> -Butyro- <i>o</i> -toluidide ...	2	58·66	0·207
† <i>n</i> -Butyro- <i>p</i> -toluidide ...	3	18·53	0·656
<i>iso</i> Butyranilide	7	30·68	0·395
<i>iso</i> Butyro- <i>o</i> -toluidide ...	2	125·71	0·096
† <i>iso</i> Butyro- <i>m</i> -toluidide ..	2	41·90	0·290
† <i>iso</i> Butyro- <i>p</i> -toluidide ...	2	44·01	0·276

† Solution not quite complete.

Effect of Chlorine.

In the ortho- and para-positions the influence of chlorine is very slight, and may either increase or retard hydrolysis. The apparent inhibitory action of chlorine in the para-position in acetanilide and propionanilide is probably due to the fact that these compounds take longer to dissolve than the ortho- and meta-isomerides.

Compound.	Number of measurements.	Time for decomposition, in hours.	<i>K</i> (average).
*Formanilide	6	0·14	87·1
* <i>o</i> -Chloroformanilide ...	3	0·13	91·9
* <i>m</i> -Chloroformanilide ...	3	0·14	87·1
* <i>p</i> -Chloroformanilide ...	3	0·13	88·4
Acetanilide	11	3·79	3·20
* <i>o</i> -Chloroacetanilide	9	3·91	3·10
* <i>m</i> -Chloroacetanilide ...	8	3·74	3·31
<i>p</i> -Chloroacetanilide.....	8	4·00	3·07
Propionanilide.....	12	6·29	1·93
<i>o</i> -Chloropropionanilide.	4	5·87	2·07
<i>m</i> -Chloropropionanilide	4	5·87	2·07
<i>p</i> -Chloropropionanilide.	4	8·00	1·52

Effect of Bromine.

Only one series of bromine derivatives was examined, namely, the bromoacetanilides. This substituent has very slight effect on the rate of hydrolysis when in the ortho- and meta-positions. The apparent diminution in the velocity of decomposition brought about by the introduction of bromine in the para-position is probably due to the fact that it dissolves less rapidly than its isomerides (compare *p*-chloroacetanilide and *p*-chloropropionanilide).

Compound.	Number of measurements.	Time for 50 per cent. decomposition, in hours.	<i>K</i> (average).
*Acetanilide	11	3.79	3.20
<i>o</i> -Bromoacetanilide ...	7	3.74	3.31
<i>m</i> -Bromoacetanilide ...	7	3.70	3.28
<i>p</i> -Bromoacetanilide ...	7	4.09	2.97

Effect of the Nitro-group.

The introduction of a nitro-group into the benzene nucleus has invariably an accelerating effect on the velocity of decomposition. With the formanilide derivatives the result is identical whether this group occupies the ortho- or para-positions, but with acetanilide and benzanilide derivatives the influence is greatest when the substituent group occupies the ortho-position, and next in magnitude when the para-position is concerned. In all cases the meta-substituent has an intermediate effect.

Compound.	Number of measurements.	Time for 50 per cent. decomposition, in hours.	<i>K</i> (average).
*Formanilide	6	0.14	87.1
* <i>o</i> -Nitroformanilide ...	Complete decomposition within 5 minutes.		118.9
* <i>m</i> -Nitroformanilide ...	3	0.10	118.9
* <i>p</i> -Nitroformanilide ...	Complete decomposition within 5 minutes.		
*Acetanilide.....	11	3.79	3.20
* <i>o</i> -Nitroacetanilide.....	1	Within 5 minutes	
<i>m</i> -Nitroacetanilide ...	7	2.22	5.45
* <i>p</i> -Nitroacetanilide.....	1	Within 5 minutes	
Benzanilide	Too insoluble for experiment.		
* <i>o</i> -Nitrobenzanilide ...	2	0.22	55.3
* <i>p</i> -Nitrobenzanilide ...	4	0.92	13.13

Effect of Methoxy- and Ethoxy-groups.

The introduction of these groups into the benzene nucleus has a very similar effect in both cases. When substituted in the ortho-position the result is to produce a considerable decrease in the magnitude of the velocity constant, but the decrease is much smaller

than in the case of the methyl group. There is also a slight decrease in the rate of decomposition when these groups occupy the meta-position, but when in the para-position a slight increase in the magnitude of the constant is observed in both cases.

Compound.	Number of measurements.	Time for 50 per cent. decomposition, in hours.	<i>K.</i> (average).
*Acetanilide.....	11	3·79	3·20
*Aceto- <i>o</i> -anisidide ..	7	5·50	2·28
Aceto- <i>m</i> -anisidide.....	6	4·24	2·86
Aceto- <i>p</i> -anisidide	6	3·57	3·40
Aceto- <i>o</i> -phenetidide ...	7	5·33	2·34
Aceto- <i>m</i> -phenetidide ..	6	4·19	2·90
Aceto- <i>p</i> -phenetidide ...	6	3·70	3·28

The result of this investigation is to show conclusively that the main effect of the introduction of substituent elements or groups into the anilide molecule is to bring about differences in the magnitude of the constants expressing the velocity of hydrolysis.

The numerous prolonged experiments carried out with the aid of a silver flask show that, so far as can be experimentally determined under the conditions chosen, complete decomposition could be brought about in all cases investigated. In eighteen instances the decomposition actually amounts to 100 per cent., and in those cases where this degree of hydrolysis has not been attained, there is no indication of an equilibrium, as the constants do not fall off perceptibly towards the end.

CHEMICAL LABORATORY,
UNIVERSITY OF BRISTOL.

CLVIII.—*Preparation of the Acyl Derivatives of the Aldehyde-cyanohydrins. Part I.*

By FRANCIS FRANCIS and OLIVER CHARLES MINTY DAVIS.

ONE of the authors, whilst investigating some reactions of the aldehyde-cyanohydrins, found that benzaldehyde readily gave a quantitative yield of benzoylmandelonitrile when treated with benzoyl chloride in the presence of an aqueous solution of potassium cyanide. As derivatives of this type do not appear to have been previously described, the reaction was investigated further, and it has been found that a corresponding change takes place with other aromatic aldehydes; only a few experiments were made with those of the aliphatic series, but

here also the behaviour was similar. Sufficient data have been collected to show that the decomposition may be generalised and expressed as follows :



Moreover, experiments carried out with the acid chlorides of anisic, *m*-nitrobenzoic, cinnamic, and phthalic acids, and also with ethyl chloroformate and benzenesulphonyl chloride, have shown that a general method has been found for the formation of the acyl derivatives of the aldehyde-cyanohydrins.

It seems probable that the first phase of the reaction consists in the formation of cyanohydrins by the interaction of the aldehyde and aqueous cyanide solution, and then, in the presence of the resulting free alkali, these react in the ordinary manner with the acid chloride to form acyl derivatives.

This view of the course of the reaction is borne out by the formation of the benzoyl derivatives of benzaldehydecyanohydrin and anisaldehyde-cyanohydrin by the interaction of benzoyl chloride and the corresponding cyanohydrin in the presence of aqueous potassium hydroxide, the resulting substances being identical with those prepared from the aldehyde direct by means of benzoyl chloride and cyanide solution.

Preliminary experiments have shown that the method employed may be of importance in the preparation of other types of derivatives, and that, besides potassium cyanide, other hydrolysed salts may be utilised. Investigations are now proceeding, and these, together with the detailed description of some of the substances mentioned in this paper, will be left for a further communication.

EXPERIMENTAL.

Preparation of Benzoyl Derivatives.

Benzoylmandelonitrile, $CHPh(OBz) \cdot CN$.—The calculated amounts of benzaldehyde and benzoyl chloride are shaken with an aqueous solution of potassium cyanide containing about 2 per cent. more than the amount required for the reaction. If large amounts are taken it is necessary to cool the flask in which the operation is carried out; after shaking vigorously for a few minutes the solid benzoyl derivative separates out, and is obtained pure and in quantitative yield by crystallisation from alcohol, from which it crystallises in well-formed needles melting at 63–64°. The substance is soluble in the ordinary organic solvents, and is not decomposed by prolonged boiling with dilute hydrochloric acid :

0.2164 gave 0.5986 CO_2 and 0.906 H_2O . C = 75.44; H = 4.64.

0.216 ,, 10.4 c.c. N_2 (moist) at 13° and 759 mm. N = 5.68.

$C_{15}H_{11}O_2N$ requires C = 75.94; H = 4.64; N = 5.90 per cent.

A molecular weight determination by the ebullioscopic method using benzene as solvent gave the following result :

Substance.	Solvent.	E.	M.W.
1·105	31·1	0·4°	238

$C_{15}H_{11}O_2N$ requires M.W. = 237.

The substance obtained from the interaction of mandelonitrile and benzoyl chloride in the presence of aqueous potassium hydroxide was identical with the above; it melted at 63° and an analysis gave N = 5·94 per cent.

Benzoyl-p-methoxymandelonitrile, $OMe \cdot C_6H_4 \cdot CH(OBz) \cdot CN$.

The method employed for the preparation of this derivative was, using anisaldehyde in place of benzaldehyde, identical with that previously described. The substance crystallises from alcohol in clear, colourless plates melting at 66—67° :

0·1998 gave 0·5244 CO_2 and 0·0894 H_2O . C = 71·58 ; H = 4·97.

0·5002 ,, 22·4 c.c. N_2 (moist) at 16° and 744 mm. N = 5·10.

0·2623 ,, 0·2295 Agl. OMe = 11·55.

$C_{16}H_{13}O_3N$ requires C = 71·91 ; H = 4·86 ; N = 5·2 ; OMe = 11·61 per cent.

A molecular weight determination by the ebullioscopic method, using benzene as solvent, gave the following result :

Substance.	Solvent.	E.	M.W.
1·1985	31·9	0·375°	267

$C_{16}H_{13}O_3N$ requires M.W. = 267.

A compound identical with the above (melting at 67° and containing 5·32 per cent. of nitrogen) was obtained by the action of benzoyl chloride on *p*-anisaldehyde-cyanohydrin in the presence of aqueous potassium hydroxide.

Benzoyl-o-methoxymandelonitrile, $OMe \cdot C_6H_4(OBz) \cdot CN$.

A small yield of this derivative was obtained from *o*-methoxybenzaldehyde. On recrystallisation from alcohol it melted at 87—88°

0·4462 gave 20·2 c.c. N_2 (moist) at 17° and 754 mm. N = 5·21.

$C_{15}H_{12}O_3N$ requires N = 5·2 per cent.

Benzoyl-p-tolylglycollonitrile, $C_6H_4Me \cdot CH(OBz) \cdot CN$.

A quantitative yield of this substance was obtained from *p*-tolualdehyde. On recrystallisation from alcohol it melted at 55—56° :

0·4984 gave 24·2 c.c. N_2 (moist) at 16° and 741 mm. N = 5·53.

$C_{16}H_{13}O_2N$ requires N = 5·57 per cent.

Benzoylcumylglycollonitrile, $\text{CHMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OBz}) \cdot \text{CN}$.

This derivative, prepared from cuminaldehyde, crystallises from alcohol in needles melting at 68—69°:

0.2239 gave 0.638 CO_2 and 0.128 H_2O . $\text{C} = 77.71$; $\text{H} = 6.3$.

0.3580 ,, 15.6 c.c. N_2 (moist) at 16° and 750 mm. $\text{N} = 5.00$.

$\text{C}_{18}\text{H}_{17}\text{O}_2\text{N}$ requires $\text{C} = 77.41$; $\text{H} = 6.09$; $\text{N} = 5.01$ per cent.

α-Benzoyloxy-γ-phenylisocrotononitrile, $\text{CHPh} \cdot \text{CH} \cdot \text{CH}(\text{OBz}) \cdot \text{CN}$.

Prepared from cinnamaldehyde; melts at 72—73° on crystallisation from alcohol:

0.2271 gave 0.6520 CO_2 and 0.108 H_2O . $\text{C} = 78.2$; $\text{H} = 5.2$.

0.517 ,, 24.4 c.c. N_2 (moist) at 18° and 736 mm. $\text{N} = 5.27$.

$\text{C}_{17}\text{H}_{13}\text{O}_2\text{N}$ requires $\text{C} = 77.6$; $\text{H} = 4.9$; $\text{N} = 5.3$ per cent.

Benzoyloxyhomopiperonylonitrile, $\text{CH}_2 \cdot \text{O}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CH}(\text{OBz}) \cdot \text{CN}$.

In the case of piperonal the reaction led to the production of an oily substance from which the above derivative, melting at 57°, was isolated by washing with a small amount of ether and crystallisation from alcohol:

0.452 gave 19.6 c.c. N_2 (moist) at 20° and 766 mm. $\text{N} = 5.0$.

$\text{C}_{16}\text{H}_{11}\text{O}_4\text{N}$ requires $\text{N} = 4.98$ per cent.

p-Chlorobenzoylmandelonitrile, $\text{C}_6\text{H}_4\text{Cl} \cdot \text{CH}(\text{OBz}) \cdot \text{CN}$.

This derivative, prepared from *p*-chlorobenzaldehyde, was isolated by the method described in the previous case, and on crystallisation from alcohol melted at 57—58°:

0.59 gave 26.1 c.c. N_2 (moist) at 12° and 748 mm. $\text{N} = 5.16$.

$\text{C}_{15}\text{H}_{10}\text{O}_2\text{NCl}$ requires $\text{N} = 5.15$ per cent.

Benzoyl-β-naphthylglycollonitrile, $\text{C}_{10}\text{H}_7 \cdot \text{CH}(\text{OBz}) \cdot \text{CN}$.

When *β*-naphthaldehyde was employed and the reaction carried out as previously described, only a small quantity of a red insoluble substance was obtained. On crystallisation from nitrobenzene it melts at 239° and from the analysis appears to be similar to the other derivatives of this class:

0.175 gave 0.506 CO_2 and 0.067 H_2O . $\text{C} = 78.86$; $\text{H} = 4.2$.

$\text{C}_{19}\text{H}_{13}\text{O}_2\text{N}$ requires $\text{C} = 79.4$; $\text{H} = 4.5$ per cent.

Trichlorobenzoyllactonitrile, $\text{CCl}_3 \cdot \text{CH}(\text{OBz}) \cdot \text{CN}$.

When chloral is dissolved in water containing the necessary amount of potassium cyanide and treated with benzoyl chloride, a white, semi-solid mass slowly separates; on crystallisation from a mixture of alcohol, water, and ether, a 50 per cent. yield of the derivative is obtained. It is very soluble in the ordinary organic solvents, insoluble in water, and melts at $40-41^\circ$:

0.564 gave 24.8 c.c. N_2 (moist) at 18° and 759 mm. $\text{N} = 5.07$.

0.608 „ 0.93 AgCl. $\text{Cl} = 37.8$.

$\text{C}_{10}\text{H}_6\text{O}_2\text{NCl}_3$ requires $\text{N} = 5.02$; $\text{Cl} = 38.24$ per cent.

*Preparation of Anisoyl Derivatives.**p-Anisoylmandelonitrile*, $\text{CHPh}(\text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}) \cdot \text{CN}$.

Anisoyl chloride can replace benzoyl chloride and the reaction is carried out in a similar manner to that previously described. The mandelonitrile derivative may be obtained pure by crystallisation from alcohol and melts at $58-59^\circ$:

0.555 gave 26.0 c.c. N_2 (moist) at 16° and 748 mm. $\text{N} = 5.37$.

$\text{C}_{16}\text{H}_{12}\text{O}_3\text{N}$ requires $\text{N} = 5.26$ per cent.

p-Anisoyl-p-methoxymandelonitrile,
 $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}) \cdot \text{CN}$.

This was prepared from anisaldehyde and crystallised from alcohol; it melts at $69-70^\circ$:

0.2570 gave 10.6 c.c. N_2 (moist) at 12° and 759 mm. $\text{N} = 4.88$.

$\text{C}_{17}\text{H}_{15}\text{O}_4\text{N}$ requires $\text{N} = 4.71$ per cent.

*Preparation of a Phthalyl Derivative.**Phthalylmandelonitrile*, $\text{CN} \cdot \text{CHPh} \cdot \text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{O} \cdot \text{CHPh} \cdot \text{CN}$.

This compound was prepared from benzaldehyde in a similar manner to the previous derivatives by using phthalyl chloride; after crystallisation from a mixture of benzene and light petroleum it melts at 120° :

0.212 gave 0.0826 H_2O and 0.5606 CO_2 . $\text{C} = 72.12$; $\text{H} = 4.33$.

0.154 „ 9.4 c.c. N_2 (moist) at 21° and 765 mm. $\text{N} = 6.99$.

$\text{C}_{24}\text{H}_{16}\text{O}_4\text{N}_2$ requires $\text{C} = 72.72$; $\text{H} = 4.04$; $\text{N} = 7.1$ per cent.

Preparation of Cinnamoyl Derivatives.

Cinnamoylmandelonitrile, $\text{CHPh}(\text{O}\cdot\text{CO}\cdot\text{CH}\cdot\text{CHPh})\cdot\text{CN}$.

A good yield of this derivative is obtained by the action of cinnamoyl chloride on benzaldehyde in the presence of aqueous potassium cyanide; when crystallised from dilute alcohol it melts at $47-48^\circ$:

0.486 gave 23.2 c.c. N_2 (moist) at 17° and 755 mm. $\text{N} = 5.5$.

$\text{C}_{17}\text{H}_{13}\text{O}_2\text{N}$ requires $\text{N} = 5.32$ per cent.

Cinnamoyl-p-methoxymandelonitrile,
 $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{O}\cdot\text{CO}\cdot\text{CH}\cdot\text{CHPh})\cdot\text{CN}$.

A small yield of this substance, melting at $86-87^\circ$, was obtained by treating the oily products of the reaction from anisaldehyde with ether and crystallising the residue from alcohol:

0.519 gave 21.6 c.c. N_2 (moist) at 16° and 752 mm. $\text{N} = 4.8$.

$\text{C}_{18}\text{H}_{15}\text{O}_3\text{N}$ requires $\text{N} = 4.77$ per cent.

Preparation of m-Nitrobenzoyl Derivatives.

m-Nitrobenzoylmandelonitrile, $\text{CHPh}(\text{O}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)\cdot\text{CN}$.

The reaction was carried out at a temperature between 40° and 50° , employing *m*-nitrobenzoyl chloride, and the derivative, when crystallised from ether, melts at $83-84^\circ$:

0.2575 gave 23.2 c.c. N_2 (moist) at 21° and 760 mm. $\text{N} = 10.21$.

$\text{C}_{15}\text{H}_{10}\text{O}_4\text{N}_2$ requires $\text{N} = 10.0$ per cent.

m-Nitrobenzoyl-p-methoxymandelonitrile,
 $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{O}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)\cdot\text{CN}$.

This derivative, prepared from anisaldehyde, on crystallisation from boiling alcohol melts at $129-130^\circ$:

0.338 gave 26.4 c.c. N_2 (moist) at 14° and 757 mm. $\text{N} = 9.15$.

$\text{C}_{16}\text{H}_{12}\text{O}_5\text{N}_2$ requires $\text{N} = 9.0$ per cent.

Preparation of a Benzenesulphonyl Derivative.

Benzenesulphonylmandelonitrile, $\text{CHPh}(\text{O}\cdot\text{SO}_2\text{Ph})\cdot\text{CN}$.

Benzenesulphonyl chloride is shaken with benzaldehyde and an aqueous solution of potassium cyanide; the resulting derivative is recrystallised from dilute alcohol and ether, and melts at 66° . On

keeping, it undergoes decomposition, the only case yet observed among the substances described in this paper :

0·6185 gave 27 c.c. N_2 (moist) at 20° and 758 mm. $N = 4\cdot97$.

$C_{14}H_{11}O_3NS$ requires $N = 5\cdot13$ per cent.

Preparation of a Carbethoxy-derivative.

Carbethoxymandelonitrile, $CHPh(O\cdot CO_2Et)\cdot CN$.

When the calculated amounts of benzaldehyde, ethyl chloroformate and aqueous potassium cyanide are shaken together and the temperature kept low, a heavy oil separates. This is extracted with ether, washed with dilute aqueous potassium hydroxide and then with water, and dried. On evaporating the ether, the oil distilled unchanged at $210\text{--}212^\circ/90$ mm., and was obtained in quantitative yield :

0·2177 gave 0·510 CO_2 and 0·1115 H_2O . $C = 63\cdot7$; $H = 5\cdot6$.

0·4895 ,, 30·2 c.c. N_2 (moist) at 21° and 762 mm. $N = 7\cdot04$.

$C_{11}H_{11}O_3N$ requires $C = 64\cdot39$; $H = 5\cdot36$; $N = 6\cdot82$ per cent.

THE CHEMICAL DEPARTMENT,
THE UNIVERSITY, BRISTOL.

CLIX.—*The Carbonates of Copper and the Cupri-carbonates.*

By SPENCER UMFREVILLE PICKERING, M.A., F.R.S.

COPPER carbonate dissolved in ammonia or in ammonium carbonate has been used for many years as a fungicide, and, more recently, the mixture obtained by adding sodium carbonate to copper sulphate has been advocated for the same purpose, notably by the Department of Agriculture and Technical Instruction for Ireland, and by various colonial authorities. This mixture is known as Soda Bordeaux. What the compound present in it is, appears, however, to be somewhat uncertain, for much of our knowledge of the carbonates of copper depends on work of rather ancient date, although the subject has been approached by several recent investigators in dealing with the double carbonates of copper and the alkali metals. What is known on the subject may be briefly summarised as follows :

The normal carbonate, CuO,CO_2 , has not been isolated, but probably exists in solution to the extent of one part in 4000—5000 of aqueous carbonic acid under several atmospheres'

pressure (Wagner, *J. pr. Chem.*, 1867, **102**, 235). Gay-Lussac (*Traité de Chimie*, Pelouze et Frémy, III, 1023) states that it constitutes the black mineral, mysorin; but this is now known to be a basic carbonate.

The green dicupric salt, $2\text{CuO},\text{CO}_2,\text{H}_2\text{O}$, identical with malachite, is the ordinary copper carbonate of commerce, and is prepared by the action of alkaline carbonates on copper sulphate. The blue precipitate obtained initially in this reaction was stated by Brunner (Pelouze et Frémy) to be malachite in a different state of hydration, but, as will be shown below, the primary precipitate consists of another basic carbonate, which becomes converted into malachite by a secondary reaction.

The blue, so-called, tricupric salt, $3\text{CuO},2\text{CO}_2,\text{H}_2\text{O}$, occurs as azurite, and is said to be manufactured by a secret process, and sold under the name of blue verditer.

A true tricupric salt, $3\text{CuO},\text{CO}_2,3\text{H}_2\text{O}$, is stated by Favre (*Ann. Chim. Phys.*, 1844, [iii], **10**, 116) to be obtained by decomposing cuprammonium carbonate with excess of water; but Favre determined only the copper and carbon dioxide in it, and it is probable that what he obtained was really the basic cuprammonium carbonate, which the present writer has obtained under somewhat similar circumstances.

By adding copper sulphate to a boiling concentrated solution of sodium carbonate, Field (*Quart. Journ. Chem. Soc.*, 1862, **14**, 70) obtained a black precipitate represented by $6\text{CuO},\text{CO}_2$, whilst Deville (*Ann. Chim. Phys.*, 1851, [iii], **33**, 104) stated that $8\text{CuO},\text{CO}_2$ is the composition of this precipitate. Evidence will be given below to show that these precipitates are not definite in composition, but consist of mixtures of copper hydroxide with undecomposed basic carbonates.

The Cupricarbonates and Double Carbonates.

A knowledge of these compounds is essential as a preliminary to the study of the carbonates of copper.

As has been known for very many years, copper may displace the hydrogen in the salts of ammonium, giving rise to cuprammonium compounds, the characteristics of which are their intense purple-blue colour, and the fact that the copper in them does not respond to the usual tests for that metal: analogous compounds are known in which the copper forms parts of the anion in carbonic and certain organic acids, becoming unrecognisable as copper by the usual tests,* and giving to the salt an

* Wood and Jones state that such solutions give the ordinary reaction with ferrocyanide; the explanation of this apparent difference of opinion will be made evident below.

intensely blue colour. The existence of these compounds has not, however, been sufficiently realised, partly because they have never received a distinctive name, and partly because they have never been isolated. They may be conveniently designated as cupricarbonates, cupritartrates, etc.

Deville (*Ann. Chim. Phys.*, 1851, [iii], **33**, 75) first described the deep blue solution which is obtained by dissolving a carbonate of copper in strong solutions of the mixed carbonate and acid carbonate of the alkali metals. This blue solution, in the case of the sodium carbonates, yields, on standing, rather light blue crystals of $\text{CuCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$,* leaving the liquid only slightly coloured; indeed, according to the present investigation, it is only when the proportion of normal sodium carbonate present is considerable that the liquid retains more than a faint trace of copper. A strongly alkaline solution of this nature was introduced by Soldiani (*Gazzetta*, 1876, **6**, 322) as a substitute for Fehling's solution in the estimation of sugar (see also Ost, *Ber.*, 1890, **23**, 1035).

The change of colour accompanying the crystallisation of the double salt is sufficient proof that the liquid cannot be a mere solution of the crystals; the latter are considerably lighter in colour than copper sulphate, whereas the liquid yielding them (as will be shown) is of a far deeper blue than the normal sulphate. Max Gröger, also (*Ber.*, 1901, **34**, 429), pointed out that the crystals will not redissolve in the mother liquor (although this statement requires slight modification), and are decomposed by water. The non-identity of the crystals and dissolved substance has been further emphasised by Reynolds (*Trans.*, 1898, **73**, 266) and by Wood and Jones (*Proc. Camb. Phil. Soc.*, 1907, **14**, 174), who proved the existence in the liquid of a highly coloured anion, and that, on electrolysis, copper is liberated at both poles. Reynolds prepared many crystalline double carbonates of potassium and other dyad metals, the majority of them containing $4\text{H}_2\text{O}$; Wood and Jones did so as well, and they note similar colour changes to those observed in the case of copper, that in the case of the cobalt compounds being specially remarkable.

The alkaline carbonates are not the only salts which form deep blue solutions with copper; the tartrates, succinates and oxalates are known to do so in the presence of excess of alkali, and it is probable that many organic salts would behave in the same way. Reference to the possible constitution of these will be made later on.

For the determination of small quantities of copper in the

* The text-books erroneously quote $6\text{H}_2\text{O}$. The writer, and others also, have found the crystals to contain $3\text{H}_2\text{O}$, retaining this water at 100° .

present investigation, the colorimetric process with ferrocyanide was adopted. Using Nessler cylinders, it is possible to detect 0.00005 to 0.00003 per cent. of copper in solution, or 0.0005 per cent. when a few c.c. are similarly examined in a test-tube. Where the copper is in the form of cupricarbonate, the alkaline liquid containing it must first be neutralised, using a scrap of litmus paper as indicator; but excess of acid interferes with the ferrocyanide reaction. For qualitative testing, the acid may be run down the side of the tube containing the liquid, when, if cupricarbonates are present, a red ring forms in the neutral zone.

The cupricarbonates give a clear yellow colour with potassium ferrocyanide, but as the change between them and copper carbonate seems to be a reversible one, the red colour of copper ferrocyanide gradually appears on standing, after a time varying between a few seconds and many hours, according to circumstances.

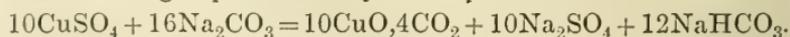
The Reaction between Copper Salts and Sodium Carbonates.

When sodium carbonate and copper sulphate solutions are mixed, some carbon dioxide is evolved, and a bulky, blue precipitate is thrown down.

To ascertain its composition, the carbonate was added to a solution of copper sulphate sufficiently weak to ensure the retention of any carbon dioxide liberated (0.05 per cent. of copper), and alkalinity was found to be attained when 1.61 molecules of sodium carbonate had been added for every molecule of copper sulphate present (mean of four concordant determinations).

Various quantities of sodium carbonate were then added to the same amounts of copper sulphate, the solutions filtered immediately, and tested for copper. By a series of approximations, it was found that the precipitation was practically complete when the carbonate amounted to (exactly) 1.6 molecules. As this coincides with the appearance of alkalinity, the reaction evidently is a simple one, and does not occur in two stages, as when an alkali hydroxide is added to copper sulphate, in which case the whole of the metal is first precipitated to form one basic sulphate, and this reacts with a further addition of alkali to form a more basic one before the liquid finally becomes alkaline (Pickering, *Trans.*, 1907, **91**, 1982)

The precipitate was found to contain no traces of sulphate unless the copper was only partly precipitated, and then in only minute quantities; its formula, therefore, is, presumably, $5\text{CuO}, 2\text{CO}_2$, its formation being represented by the equation:



This was verified by determining the amount of sodium hydroxide

carbonate in an aliquot portion of the filtrate: the mean of the two determinations gave exactly 12NaHCO_3 for every 10CuSO_4 taken. None of the sodium carbonate, therefore, is retained in combination with the precipitate. [This could not have been ascertained satisfactorily by examining the precipitate, as washing it would probably have removed any sodium carbonate combined with it, as in the analogous cases of the basic sulphates.]

The precipitation of copper, it was said above, was practically complete when 1.6 molecules of sodium carbonate had been added to each molecule of copper sulphate; it is never absolutely so, because the basic carbonate dissolves in the sodium hydrogen carbonate formed in the reaction; but the quantity present when dealing with very dilute solutions is barely recognisable. Where more than 1.6 molecules of sodium carbonate are added, the amount of copper dissolved becomes more considerable, and with stronger solutions the liquid becomes quite blue. Exposure to the air, by increasing the proportion of acid carbonate present, increases the amount of copper dissolved.

On heating strong solutions of copper sulphate and sodium carbonate, the precipitate speedily blackens, and after prolonged boiling it contains only traces of carbonate. To ascertain whether confirmation could be obtained of Field's statement that $6\text{CuO},\text{CO}_2$ is formed in this way, or of Deville's, that $8\text{CuO},\text{CO}_2$ is formed, copper sulphate solution was added to a boiling concentrated solution of sodium carbonate, and some of the precipitate removed after two, ten, and thirty minutes; these portions, after drying at 100° , were found to contain 94.1, 94.9, and 96.5 per cent. of CuO , respectively, thus indicating a continuous decomposition; all of them were more basic even than $8\text{CuO},\text{CO}_2$, which contains 93.5 per cent. of CuO .

The Carbonate, $5\text{CuO},2\text{CO}_2$.

The carbonate obtained as above is of a full blue colour, and rather watery in appearance, being quite different from the lighter blue and more opaque basic sulphates, and from the other blue basic carbonates to be described immediately. Although it is decomposed when heated in a moist condition, it can be dried over sulphuric acid (when it contracts to a brittle, dark blue mass), and may then be heated to 100° without decomposition. After drying thus, it is dark green, and contains $3\text{H}_2\text{O}$ (Found, $\text{H}_2\text{O} = 10.36$; $5\text{CuO},2\text{CO}_2,3\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 10.00$ per cent.). It retains this colour on cooling in dry air, but on exposure to moist air it becomes blue again.

The carbonate, $5\text{CuO},2\text{CO}_2$, may be deprived of its carbon

dioxide entirely, forming copper hydroxide, by leaving it in contact with cold saturated sodium carbonate solution for some days or weeks, according to the temperature. On the other hand, it readily takes up more carbon dioxide if left in contact with a solution of sodium hydrogen carbonate for some days, the precipitate contracting to a compact, green powder, which is malachite, $2\text{CuO}, \text{CO}_2, \text{H}_2\text{O}$. This change is evidently not a direct one, and is preceded by the partial dissolution of the basic sulphate in the liquid, for this becomes more or less blue, and the malachite deposited is found to adhere to the containing vessel, and to consist of spheres of great regularity, often resembling a very uniform emulsion. After long standing, these spheres collect together, by redissolution and redeposition, in circular masses, suggesting the botroïdal formation of natural malachite.

When washed on the filter with well-boiled water, or with a weak solution of normal sodium carbonate, $5\text{CuO}, 2\text{CO}_2$, it gives no trace of copper to the liquid, but it does so with aqueous carbonic acid, although to a smaller extent than with a solution of sodium hydrogen carbonate, and is converted by it, as by the acid carbonate, into malachite. It is probably the normal copper carbonate and a double carbonate of copper and sodium which constitute the soluble primary products in these two cases, respectively.

In spite of the insolubility of the basic carbonate in normal sodium carbonate, the addition of this latter to a mixture of the basic carbonate with sodium hydrogen carbonate increases the amount of copper passing into solution, and deepens the colour of the liquid. This is due to the formation of α -cupricarbonate, as will be explained below (p. 1422).

The basic carbonate generally changes into malachite if left in the mixed liquid from which it had been precipitated, and more readily the more nearly the amount of sodium carbonate used for its precipitation approximates to that required by the equation given on page 1412.

The Reaction between Copper Sulphate and Acid Sodium Carbonate, $5\text{CuO}, 3\text{CO}_2$.

When weak solutions (0.05 per cent. of copper) are taken, the addition of sodium hydrogen carbonate to copper sulphate throws down rather gradually a light blue, opaque and finely divided precipitate, which is very different in appearance from that given by the normal carbonate. In the accompanying table are entered the results of a series of experiments with different proportions of the reagents, the total volumes of the liquids being the same in all cases.

The precipitation of the copper is never complete, but reaches a maximum of 92—93 per cent. when three molecules of sodium hydrogen carbonate, or more, are present for every molecule of copper sulphate. The amount of acid carbonate used up for the copper precipitated is always more than two equivalents, and, with the exception of the extreme experiments—probably with the exception only of the last three experiments, as the first one is uncertain owing to the smallness of the precipitate obtained—is practically constant at about 2.15 molecules of sodium hydrogen carbonate for every molecule of copper sulphate. The only way in which more than two molecules of sodium hydrogen carbonate can be used up is by the precipitate combining with additional sodium carbonate, and some perplexity was caused by not being able to find any alkaline carbonate in the washed precipitate. It was ascertained eventually that such carbonate was present, but was given up at once on washing. The examination was made by measuring the liquids after mixing them, and again after filtration; by then making an assumption, which could not be far from the truth, as to the density of the precipitate, the amount of liquid mechanically retained by the latter could be calculated. The precipitate was then washed, and the alkali determined, both in the original filtrate and in the washings, when it was found that the latter contained the missing alkali.

TABLE I.

Precipitation of Copper Sulphate by Acid Sodium Carbonate.

	Mols. NaHCO ₃ added to 1 mol. CuSO ₄ .	Mols. CuSO ₄ precipitated.	Mols. NaHCO ₃ used for 1 mol.-atom Cu in precipitate.	Composition of the precipitate.		
				CuO.	SO ₃ .	CO ₂ .
1.	0.41	0.123	2.77	—	—	—
2.	0.82	0.307	2.23	—	—	—
3.	1.00	—	—	76.133	2.603	21.265
4.	1.64	0.660	2.13	—	—	—
5.	2.00	—	—	74.816	2.743	22.441
6.	2.46	0.890	2.12	—	—	—
7.	2.87	0.922	2.11	—	—	—
8.	3.28	0.933	2.13	—	—	—
9.	3.69	0.913	2.15	—	—	—
10.	4.00	—	—	76.829	0.819	22.322
11.	4.10	0.908	2.16	—	—	—
12.	5.36	0.928	2.12	—	—	—
13.	6.00	—	—	75.912	0.555	23.535
14.	6.56	0.926	2.23	—	—	—
15.	9.84	0.925	2.29	—	—	—
16.	12.30	0.892	2.41	—	—	—
17.	16.43	0.888	2.69	—	—	—

Besides sodium carbonate, the precipitate contains considerable quantities of basic sulphate, especially when the precipitation of

the copper is less complete. Analyses of the washed precipitates obtained in four cases are given in the table. On the assumption that the SO_3 is present as the lowest basic sulphate of copper, $4\text{CuO},\text{SO}_3$ (any other assumption gives less concordant results), the composition of the basic carbonate of copper is found to be 10CuO , with 5.85CO_2 , 6.18CO_2 , 5.50CO_2 , and 5.78CO_2 , respectively. The mean of these gives $10\text{CuO},5.8\text{CO}_2$, which is, within the limits of error in such a case, $5\text{CuO},3\text{CO}_2$. That this carbonate should combine in a loose fashion with some of the sodium carbonate is analogous to what occurs in the case of the basic sulphates (Pickering, Trans., 1907, **91**, 1991).

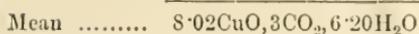
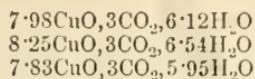
This carbonate can be dried without any signs of decomposition, and it then forms a light blue powder, quite different from the dark, brittle $5\text{CuO},2\text{CO}_2$. On heating at 100° , it remains blue, and then retains about $7\text{H}_2\text{O}$. On boiling with water, it gradually blackens, as all the other basic carbonates do.

When concentrated solutions of copper sulphate and sodium hydrogen carbonate are mixed, considerable quantities of carbon dioxide are evolved, and the light blue precipitate formed re-dissolves, producing a deep blue liquid; warming increases the amount of copper which can be thus dissolved, but on boiling, or before, the substance in solution decomposes rather suddenly, forming a green precipitate of malachite, and leaving the liquid only slightly blue. This decomposition often takes place during, or after, filtering; but, if it does not do so then, the dark blue solution decomposes in another manner, depositing gradually throughout twenty-four hours, or more, fairly light blue crystals of the double salt, $\text{CuSO}_4,\text{Na}_2\text{CO}_3,3\text{H}_2\text{O}$, and leaving the liquid with often only a trace of copper in it. These changes will be dealt with more fully below.

The basic carbonate, $5\text{CuO},3\text{CO}_2$, just like $5\text{CuO},2\text{CO}_2$, dissolves slightly in aqueous carbonic acid, but is insoluble in the normal carbonate and in pure water.

The Carbonate, $8\text{CuO},3\text{CO}_2,6\text{H}_2\text{O}$.

When the crystals of the double salt just mentioned are washed, they retain their form, but become opaque, and are found to have parted with the whole of the sodium carbonate present in them, but none of the copper. The residue is of a rather dark blue colour, and, when dried at 100° , becomes green. It is quite unlike any of the other three basic carbonates, and is evidently a definite compound. Analyses of three different preparations of it gave the formula as:



The weight became constant rather slowly at 100° , and one of the samples evidently still retained an appreciable excess of water.

This basic carbonate behaves like the others towards solutions of sodium carbonate, sodium hydrogen carbonate, and carbon dioxide; and a similar behaviour is exhibited by the crystalline double carbonate.

Tricupric Carbonate.

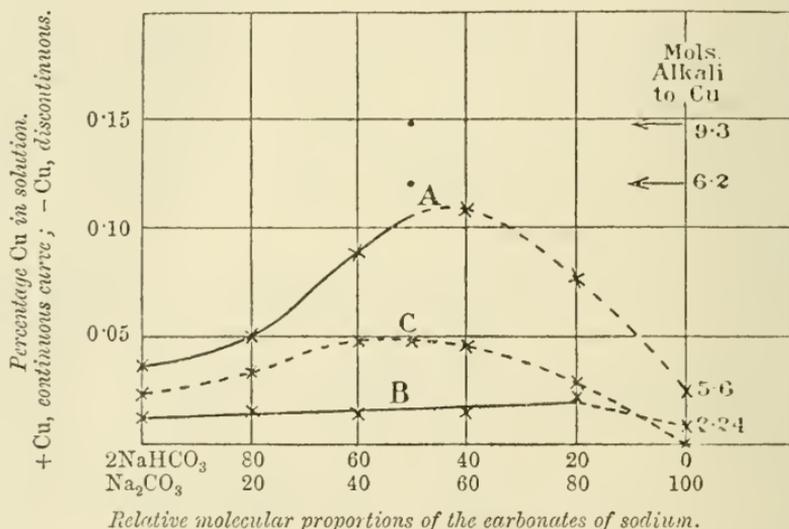
Attempts to prepare tricupric carbonate by the method employed by Favre (*loc. cit.*) failed. Malachite was digested for two days at 25° with a concentrated solution of ammonium carbonate; but the deep purple liquid thus obtained gave no precipitate at all on dilution. On adding alcohol, a few small crystals of a purple colour, very soluble in water, were obtained on one occasion, these evidently being a cuprammonium salt; on another occasion a good crop of shining, purple, crystalline plates was obtained. These were quite insoluble in water, and consisted, apparently, of a basic cuprammonium carbonate.

When concentrated solutions of copper sulphate and ammonium carbonate were mixed, a deep purple solution was obtained, which, on heating, gave some precipitate of malachite, and, on dilution, gave a bulky, blue precipitate, which proved to be a basic sulphate of the formula $15\text{CuO}, \text{SO}_3$. The addition of alcohol gave, in one instance, a few blue crystals, which were insoluble in water, and evolved some ammonia on heating, being probably a double copper ammonium carbonate analogous to the double copper sodium carbonate; but, generally, dilution with alcohol gave only a crop of crystalline needles of cuprammonium sulphate.

The basic sulphate just mentioned has not been obtained before. The analytical values were $\text{Cu} : \text{SO}_3 = 15 : 0.985$. It is noticeable that such a sulphate bears a very simple relation to two of the other basic sulphates already known, namely, $10\text{CuO}, \text{SO}_3$ and $5\text{CuO}, \text{SO}_3$ (Pickering, *Trans.*, 1907, **91**, 1982). Attention has previously been drawn to the predominance of 5 as the coefficient of the equivalents of metallic oxide in basic sulphates in general. The new sulphate, $15\text{CuO}, \text{SO}_3$, can be dried by heat without any blackening, and, therefore, contains no uncombined hydroxide.

*The Soluble Copper Compounds.**Double Carbonate and Cupricarbonate.*

To gain further information as to the nature of the changes accompanying the dissolution of copper carbonate in alkaline liquids, the same volume of copper sulphate solution was added to a constant volume of a solution of alkali, consisting of normal and acid sodium carbonates in different proportions. In one case (first half of table II) the molecular proportion of the two carbonates (representing the molecule of acid carbonate as $\text{Na}_2\text{H}_2(\text{CO}_3)_2$) was 5.6 times that of the copper sulphate; in the other (lower half of the table), it was only 2.24. The total volumes of the mixed liquids were the same throughout each series, but



were different in the two series, the solutions being taken of the maximum possible strength consistent with avoiding any separation of sodium carbonate at the temperature of the experiments, which was 22°. Some of the liquid was removed after various intervals of time, and filtered, and the amounts of electropositive and electronegative copper in it determined.

The first set of observations, made five minutes after the mixing, shows that, so long as the acid sodium carbonate predominates, all the copper in solution is electropositive, but that, as the proportion of normal carbonate is increased, electronegative copper appears, and soon becomes the sole product. The significance of the letters *D* and *M* will be explained below.

This is seen better in the curves *A* and *B* in the accompanying

figure, where the percentage of copper in solution is plotted against the proportion in which the two sodium carbonates are added, the

TABLE II.

Copper Sulphate added to Mixtures of Normal and Acid Sodium Carbonates.

(The + and - signs indicate nature of the copper in solution.)

	Mols. alkali to each Cu taken.		Percentage of total copper dissolved.	Actual percentage of copper in liquid after :			
	Na_2CO_3 .	2NaHCO_3 .		5 minutes.	24 hours.	48 hours.	72 hours.
<i>Series I, with $\text{CuSO}_4 + 5.6 \left\{ \begin{array}{l} \text{Na}_2\text{CO}_3 \\ 2\text{NaHCO}_3 \end{array} \right\} + 300\text{H}_2\text{O}$.</i>							
1.	0.00	5.6	9	+0.036	+0.040	+0.003M	—
2.	1.12	4.48	12	+0.050	+0.022 ^D _M	+0.002M	—
3.	2.24	3.36	23	{ +0.072 -0.016	+0.004 ^D	+0.001 ^M	—
4.	3.36	2.24	26		-0.108	-0.016 ^D	-0.002 ^D
5.	4.48	1.12	18	-0.076 ?	-0.058	-0.054	-0.032 ^D
6.	5.6	0.00	6	-0.026	-0.022	-0.022	-0.023
<i>Series II, with $\text{CuSO}_4 + 2.24 \left\{ \begin{array}{l} \text{Na}_2\text{CO}_3 \\ 2\text{NaHCO}_3 \end{array} \right\} + 400\text{H}_2\text{O}$.</i>							
7.	0.00	2.24	1.5	+0.013	+0.013	+0.002M	—
8.	0.45	1.79	2.0	+0.016	trace M	—	—
9.	0.90	1.34	1.9	+0.015	+0.015	+0.001M	—
10.	1.34	0.90	2.0	+0.016	+0.014	+0.007 ^D	—
11.	1.79	0.45	2.5	+0.021	+0.021	+0.001M	—
12.	2.24	0.00	1.1	-0.009	-0.027	—	-0.018 *

* Malachite appearing after ten days.

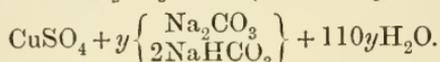
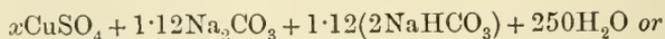
dotted portions of the curves representing the results wherein the copper is electronegative. The variation in the amount of copper passing into solution is continuous throughout, showing no abrupt change when electropositive copper gives place to electronegative.

The point at which this change occurs seems to depend solely on the proportion of normal sodium carbonate to copper. This is shown more clearly by the series of experiments in table III, wherein this ratio was altered, while the proportion in which the two carbonates were used was kept constant. This set of experiments and the first series in table II give, respectively, 3.3 and 2.2 molecules of sodium carbonate added for every molecule of copper sulphate as the point at which electronegative copper appears, or 11 and 13 molecules of sodium carbonate for every atom of copper passing into solution, although the ratio of normal carbonate actually in the liquid would be rather lower, owing to some carbon dioxide being given off in the precipitation of the basic salt.

The amount of copper passing into solution evidently depends on the relative proportion of the two sodium carbonates present, but, with any given mixture of these, it is directly proportional to the total carbonate present. On plotting out the values in table III, they are found all to lie on a straight line up to 18.7 molecular proportions of the carbonates, at which point the dissolution of the copper taken becomes complete. The total amount of copper which can be obtained in such solutions reaches about 0.15 per cent., and this has never been exceeded in any of the present experiments.

TABLE III.

Copper Sulphate added to Equimolecular Mixtures of Normal and Acid Sodium Carbonate.



	<i>x.</i>	<i>y.</i>	Percentage of total copper dissolved.	Actual percentage of copper in liquid after :			
				5 minutes.	24 hours.	48 hours.	72 hours.
1.	0.72	3.1	5	+0.043	+0.034	+0.033 <i>M</i>	-0.003
2.	0.60	3.7	8	+0.060	{ +0.050 -0.015	+0.004 -0.005 <i>D</i>	+ ? <i>D</i> -0.006 <i>M</i> }
3.	0.48	4.7	16	{ + ? -0.094	+0.045 -0.048 <i>D</i>	+0.007 <i>D</i> -0.004 <i>M</i>	+0.0 <i>D</i> -0.006 <i>M</i> }
4.	0.36	6.2	27	-0.120	-0.050 <i>D</i>	-0.009 <i>D</i>	— <i>D</i>
5.	0.24	9.3	50	-0.148	-0.080	-0.010 <i>D</i>	— <i>D</i> <i>M</i> }
6.	0.12	18.7	100	-0.128 <i>D</i>	-0.018 <i>D</i>	-0.016 <i>D</i>	— <i>D</i>
7.	0.04	56.0	100	-0.043	-0.024 <i>D</i>	-0.016 <i>D</i>	— <i>D</i>

The highest two results from table III are inserted in the diagram.

A rise in temperature increases slightly the amount of copper passing into solution, and an increase in the dilution reduces it, whilst the proportion of the dissolved copper which is in the electronegative condition is increased, both by rise of temperature and by dilution, very conspicuously so by the former. These facts are illustrated by the following observations made with a solution of the same composition as No. 3 in table II:

Passing into solution.	Percentage of total copper.	Percentage of the dissolved copper which is electronegative.
At 5°	19	0
At 20°	20	6
At 50°	25	71

Passing into solution.	Percentage of total copper.	Percentage of the dissolved copper which is electronegative.
With 80 H ₂ O	14	0
„ 600 H ₂ O	11	2.5
„ 900 H ₂ O	10	12
„ 1500 H ₂ O	7	16
„ 6300 H ₂ O	3.6	24

Whether the dissolved copper is in the electropositive or electronegative form, all these solutions are intensely blue, the depth of colour being far greater than that of copper in the form of sulphate, although the quality is the same, and quite unlike the violet of the cuprammonium compounds. By direct comparison, the colour of the compound containing electropositive copper was found to be 30 times more intense than that of copper in copper sulphate, whilst that with electronegative copper was 80 times more intense.

The various solutions recorded in tables II and III, together with the precipitates contained in them, undergo a marked change when kept for a day or two, this change consisting in the formation of either malachite or of the crystalline copper and sodium carbonate, sometimes of both together. These substances are deposited from the solution, and at the same time most, or all, of the basic carbonate present is likewise changed into them, the liquid becoming almost colourless, and retaining only a trace of copper. The change is a rapid one, but not instantaneous. The appearance of malachite is indicated in the tables by *M*, and that of the double salt by *D*. The copper finally remaining in solution is generally greater when malachite is formed than when the double salt is the product; the results in series II of table II, and those in table III, show this best.

Whether malachite or the double salt is formed seems to be determined to some extent by arbitrary conditions, but, as a rule, the former appears first in, or is the sole product from, solutions containing electropositive copper, and the double salt from those containing electronegative copper; thus, of seven instances in the tables where malachite was the prime or sole product, the copper was electropositive in six of them, whilst out of ten instances where the double salt was the prime or sole product, seven are cases where the dissolved copper was electronegative. Many other instances of a similar character were observed. Some malachite often appears after the double salt has begun to crystallise, and it would seem as if the crystals themselves sometimes become converted into malachite (see No. 3 in table II). Where the amount of copper in solution is small, and that of sodium carbonate large, as in No. 6, table II, no formation of either malachite or double salt occurs, even after many weeks; where such conditions

are approximated, as in Nos. 5 and 12, the formation of these substances is much retarded. With larger proportions of normal carbonate present, the amount of electronegative copper retained permanently in solution could, no doubt, be increased beyond the maximum reached in any of these experiments (0.023 per cent. in No. 6), but such solutions would not be permanent when exposed to the carbon dioxide in the air.

It is possible now to explain the somewhat puzzling reactions occurring when a concentrated solution of copper sulphate is added to a concentrated solution of sodium hydrogen carbonate. The basic carbonate, $5\text{CuO}, 3\text{CO}_2$, is first precipitated, and then gradually absorbs carbon dioxide from the sodium hydrogen carbonate present, passing into solution as the normal copper carbonate, or, rather, as a double carbonate of copper and sodium, forming a deep blue liquid wherein the copper is electropositive. On standing, this soluble compound gives rise either to the crystalline double carbonate, or else decomposes into malachite, nearly all the copper going out of solution. On heating to the boiling point, the change into malachite always takes place if the solution contains much copper. If the light blue liquid and the malachite resulting from this change are boiled together for some time, the proportion of normal sodium carbonate in the liquid is increased, and the precipitate gradually redissolves, forming again a deep blue liquid, but one in which the copper is now electronegative, being present in the form of cupricarbonate. This liquid, on standing, nearly always yields the crystalline double carbonate, and not malachite.

The change from the soluble compound with electropositive copper, into the cupricarbonate, with electronegative copper, is a reversible one. On taking a rather weak solution of the former and heating it to boiling, it becomes darker, and the copper no longer reacts with ferrocyanide; but, on cooling, it becomes lighter again, and responds to the ferrocyanide test.

The experiments 6 and 12 of table II, wherein no sodium hydrogen carbonate was added, present no difficulty in accepting the preliminary step in the dissolution of the copper as being the formation of normal copper carbonate from the basic carbonate and sodium hydrogen carbonate, for some of the latter will have been formed during the precipitation of the basic salt. It is found, however, that any of the basic carbonates, after being thoroughly washed, will gradually dissolve to form cupricarbonate when boiled with a concentrated solution of sodium carbonate; even ignited copper oxide will do the same. It is probable that, in such cases, the carbon dioxide necessary to convert them into normal copper carbonate is derived from the partial decomposition

of the sodium carbonate into hydroxide and carbon dioxide. Such a decomposition has been shown to occur readily by fusion (Pickering, Trans., 1887, 51, 72), and it need occur only to a minimal extent in a boiling solution to account for the facts; since the products (both sodium hydroxide and carbon dioxide, on the view suggested below) would be utilised at once to form the cupricarbonate.

The cupricarbonate has the power of oxidising dextrose with the precipitation of cuprous oxide. This action takes place in the cold, or, more rapidly, on heating, and is preceded by the formation of some soluble compound of the cupricarbonate with the sugar, for the amount of copper passing into solution at first is greatly increased by the sugar. No such action, nor any precipitation of cuprous oxide, occurs when the soluble compound present is that containing electropositive copper.

Action of Sodium Hydroxide.

When sodium hydroxide is added to a solution of copper carbonate in sodium hydrogen carbonate, the latter becomes converted into normal sodium carbonate, and the same result is obtained as if excess of sodium carbonate is added, namely, the formation of the cupricarbonate; but when the amount of sodium hydroxide is further increased, it abstracts carbon dioxide from this cupricarbonate, and a blue basic carbonate of copper is precipitated, leaving only a trace of copper in the solution. This precipitate is evidently a mixture, as it blackens in parts on drying at 100° , and three different preparations of it were found to contain, after drying, copper oxide varying between 76.3 and 90.2 per cent.

On adding still further excess of sodium hydroxide, this precipitate again dissolves, to form a deep violet-blue liquid, the dissolution becoming complete when about 300 molecules of sodium hydroxide are present for every atom of copper. The coloration is more intense than that of the cupricarbonate, being about 200 times deeper than that of copper in the form of sulphate, although accurate comparison is impossible, owing to the difference in the tone of the colour. A similar solution may be obtained by digesting any of the copper carbonates with concentrated sodium hydroxide. This liquid, in which the copper is also electronegative, appears to be quite stable, and does not give rise to malachite or the crystalline double carbonate, as the cupricarbonate does. The strongest solution of it which has been obtained contained 0.4 per cent. of copper. On dilution with a large excess of water, a basic carbonate is thrown down, but the copper in solution remains

electronegative; dilution with a smaller amount of water gives a slight precipitate of copper hydroxide, due, no doubt, to the secondary reaction of the excess of alkali on the basic carbonate first deposited. Prolonged boiling also results in the precipitation of some hydroxide, but about 0.2 per cent. of copper remains permanently in solution.

This compound also oxidises dextrose, with the precipitation of cuprous oxide, and, moreover, it has the property of combining with cellulose. On filtering through paper, all the copper is retained by the paper, as if it were present as an insoluble precipitate. Likewise a piece of filter paper shaken up with the liquid renders the latter colourless, the paper becoming violet-blue. When, however, the latter is washed, the excess of alkali necessary for the existence of the copper compound is removed, and only a basic carbonate of copper is left, the paper appearing to have been unaffected by the changes.

The existence of these soluble copper compounds explains why the results obtained in the determination of copper by precipitation with potassium hydroxide nearly always give values which are too low, for the potash generally contains carbonate, and one or other of these soluble compounds with electronegative copper will be formed. Added to this, it may be mentioned, copper hydroxide has been found to dissolve in ordinary distilled water to the extent of one part in 800,000.

Nature of the Soluble Compounds.

It has been assumed by Reynolds, and by Wood and Jones (*loc. cit.*), that the deep blue compound in a solution of copper in sodium carbonate has the same empirical formula as the double carbonate which crystallises from the liquid. No evidence, however, has been brought forward to prove this, and very little is afforded by the present work. That the basic carbonates require the addition of carbon dioxide before they will dissolve shows that the proportion of $\text{CuO} : \text{CO}_2$ in the soluble compounds is greater than it is in the basic carbonates themselves; its decomposition by heat (which would tend to deprive it of carbon dioxide) into the basic carbonate is also in accordance with this view; it is probable, too, that the two soluble compounds have very similar formulæ, as the passage of the one into the other does not affect the regularity of the curves representing their formation (p. 1420).

As regards the soluble compound containing electronegative copper (the cupricarbonate), somewhat stronger evidence has been obtained, as follows: If the compound in solution has the same formula as the double carbonate, its formation from malachite would result from an interaction with the two sodium carbonates

in equimolecular proportions (taking 2NaHCO_3 as the molecule), thus:

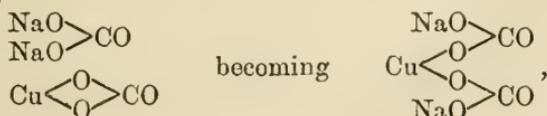


Now, when one gram of malachite was digested for twenty-four hours at 18° with 100 c.c. of a concentrated solution containing 5 molecular proportions of the mixed carbonates, the percentage of copper passing into solution (which was electronegative in all cases) was found to be that represented in curve *C* in the figure on p. 1418, the maximum (0.048 per cent.) being attained when the two carbonates were present in about equimolecular proportions, as required by the above equation; the actual position of the maximum is at about 55 per cent. of the acid carbonate, the slight excess of this which has thus been required being, no doubt, due to the malachite having contained a little of the more basic carbonate, $5\text{CuO},2\text{CO}_2$. A similar position of the maximum is seen in the curve *A*, but here it is shifted somewhat in the other direction, as there was a loss of some carbon dioxide from the liquid in the formation of the basic carbonate, as already explained. In the case of curve *B*, the shifting of the maximum is very great, as a similar loss of carbon dioxide would leave but little normal sodium carbonate in the liquid.

The similarity of the curves *A* and *C*, especially as regards the concavity of the first portions, is noteworthy.

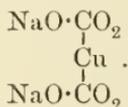
Assuming that the crystalline double salt and the two soluble compounds have all the same empirical formula, we may assign to the crystalline salt the constitution of a molecular compound, $\text{CuCO}_3,\text{Na}_2\text{CO}_3$. In colour, it is intermediate between an ordinary blue copper salt and a colourless salt, and in this respect closely resembles the double sulphates. With these, the evidence that they are simply additive compounds is strong, for their specific heats are very nearly the sum of the specific heats of the component sulphates (Pickering, *Trans.*, 1886, **49**, 12). Some of the double sulphates, for example, magnesium potassium sulphate, are decomposed by water, like the copper sodium carbonate, whereas others are stable in solution, for example, the copper potassium sulphate, but such differences are simply a question of the magnitude of the thermal changes involved (*loc. cit.*, p. 15).

To explain the existence of an isomeride of the double carbonate, but one still containing copper in the electropositive condition, the transposition of the copper and sodium atoms would appear to be satisfactory:



and the second compound may be conveniently termed a sodio-cupric carbonate to distinguish it from the double salt.

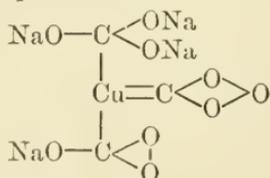
In the other soluble isomeride, the cupricarbonate, the copper is electronegative, and cannot, therefore, be regarded as replacing hydrogen in hydroxyl; the only alternative is that this must be united directly with the carbon, just as in the analogous cuprammonium compounds it is united directly with the nitrogen. This may be represented by:



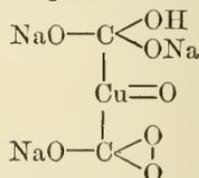
Such a representation is, however, not altogether sufficient, for it does not explain why a large excess of carbonate should be essential for its existence, nor why it should act as an oxidising agent, and decompose with the formation of cuprous oxide. There is, also, the existence of a fourth compound of a similar nature, obtained by sodium hydroxide, to be reckoned with.

The difficulties may be removed by supposing the copper atom to act as a tetrad, and to attach to itself either the oxygen from sodium hydroxide, or the CO_3 from Na_2CO_3 , whilst the other oxygen atoms in the molecule become converted into hydroxyl, for which, we know, there is a strong tendency in the case of all carbonates. The two compounds would then become:

α -Cupricarbonate.



β -Cupricarbonate.



the α -cupricarbonate being the compound formed by the action of excess of sodium carbonate on the sodiocupric carbonate ($=\text{Na}_2\text{Cu}(\text{CO}_3)_2 + \text{Na}_2\text{CO}_3$), and the β -cupricarbonate being that formed by excess of sodium hydroxide ($=\text{Na}_2\text{Cu}(\text{CO}_3)_2 + \text{NaOH}$). A doubling of the proportion of sodium carbonate or of hydroxide united with the cupricarbonate nucleus would give a more symmetrical form to the molecules. Both formulæ represent the presence of loosely attached atoms of oxygen, which would be readily given up to an oxidisable substance like dextrose, leaving a residue with excess of sodium or hydrogen atoms, the result of which would be the reduction of the copper to cuprous oxide. The formula for the α -cupricarbonate, also, well expresses its decomposition by sodium hydroxide, carbon dioxide being abstracted from it, and a basic carbonate being produced in consequence.

Fehling's solution evidently contains a compound analogous to one or other of the cupricarbonates, electronegative copper being present in it, and an excess of alkali being essential for its existence.

The suggestion has arisen that what is represented as the β -cupricarbonate may really be a sodium cuprate; this cannot be absolutely negatived, although it is improbable. Ignited copper oxide does dissolve to form a light violet-blue solution in sodium hydroxide, even when the latter has been prepared from sodium, and with the exclusion (as far as possible) of carbon dioxide; but the amount passing into solution never exceeds 0.02 per cent. of copper, as against 0.4 per cent. obtainable when copper carbonate is dissolved in soda of the same strength. The most probable view is that the cuprate does exist, but is a different substance from that described as the β -cupricarbonate. The limiting product of the action of lime water on copper sulphate is, probably, also a cuprate, its formula being $\text{CuO}, 3\text{CaO}$ (Pickering, *Trans.*, 1907, **91**, 1991). The addition of sodium carbonate to a mixture of copper oxide and sodium hydroxide does not increase the amount of copper passing into solution.

The analogy drawn above between the double carbonates and double sulphates of copper when in the crystalline condition is, no doubt, sound, but it is questionable whether it can be legitimately pushed any further, for, although the double sulphates, like the carbonates, exist in three different modifications, the second and third modifications of them can exist in the solid condition only. When the crystalline double sulphate is dehydrated at 100° , it forms a blue powder, but this, on heating to $150\text{--}200^\circ$, becomes quite white, the change being accompanied by an evolution of as much as 3220 cal. (calculated for ordinary temperatures); the white modification, in its turn, becomes converted at $300\text{--}400^\circ$ into a green modification, which, being formed with an absorption of 1918 cal., is somewhat unstable, and easily passes back into the blue or white modifications (Pickering, *Trans.*, 1886, **49**, 1). There is, however, no evidence that the copper in any of these modifications is in the electronegative condition, and they all dissolve in water to form solutions of the ordinary double sulphate. An element like sulphur offers more facilities for diversity of arrangement in the molecule than does the carbon in the carbonates, and it is probable that the different modifications of the double sulphates are due to causes which may operate even in the case of simple sulphates, for it has been found that these, in the anhydrous and amorphous condition, may occasionally exist in two modifications, according to the temperature to which they have

been heated. Sodium sulphate is an instance in point (Pickering, Trans., 1884, 45, 686).

Nevertheless, there appear to be sulphate compounds analogous to the β -cupricarbonates. The compound with the formula $10\text{CuO}, \text{SO}_3, 4\text{CaO}, \text{SO}_3$, which is present in Bordeaux mixture (Pickering, Trans., 1907, 91, 1991), appears to be of such a nature; it is violet, instead of blue, like the other basic sulphates, it dissolves in a solution of dextrose, and ultimately oxidises it, with the precipitation of cuprous oxide, whilst, when in solution in sugar (before oxidation begins), it is absorbed by cellulose.

The cupricarbonates are evidently representatives of a very large class of compounds, and one which certainly deserves further study, for, not only do other organic acids form similar compounds, but most other dyad metals seem to be able to act like copper.

The Colour of Copper Salts.

The well-known change from blue to green of copper chloride solutions on heating or concentration has been attributed to a change in the ions by some, and by others to a change in hydration. A similar change, however, has been noticed in two of the basic carbonates here described, and also in one of the basic sulphates (Trans., 1909, 95, 127), when these are in the solid condition, the blue compounds becoming green when dehydrated, and reverting to blue when rehydrated. A change in the ions cannot apply in such cases.

Summary.

Besides the mineral azurite, $3\text{CuO}, 2\text{CO}_2, \text{H}_2\text{O}$, and the ordinary, and most stable, carbonate of copper, malachite, $2\text{CuO}, \text{CO}_2, \text{H}_2\text{O}$, the following carbonates have been isolated:

$5\text{CuO}, 2\text{CO}_2$, a blue, bulky precipitate obtained by the precipitation of copper salts by normal sodium carbonate. It loses its carbon dioxide readily when warmed in the moist condition, or when digested with a concentrated solution of sodium carbonate, but takes up more carbon dioxide, forming malachite, when digested with acid sodium carbonate.

$5\text{CuO}, 3\text{CO}_2$, or a carbonate approximating thereto, is formed, mixed with basic sulphate, by the precipitation of copper sulphate with acid sodium carbonate. It is a light blue, dense solid, more stable than the foregoing.

$8\text{CuO}, 3\text{CO}_2, 6\text{H}_2\text{O}$ is a rather dark blue carbonate, obtained by the action of water on the double carbonate of copper and sodium.

Attempts to prepare $3\text{CuO}, \text{CO}_2$ and other more basic carbonates, which have been said to exist, were not successful.

All the basic carbonates are insoluble in water and in normal sodium carbonate solution, but they dissolve slightly in aqueous carbonic acid and in acid carbonates, a normal copper carbonate, or a double carbonate of copper and the alkali metal, being formed. The latter is obtained as a rather light blue, crystalline double salt from such solutions, but it is probably a molecular compound of the two carbonates, and, as it will not redissolve in the mother liquor, and is decomposed by water, the solution yielding it must contain some compound different from, but probably isomeric with, it: $\text{NaO}\cdot\text{CO}\cdot\text{OCuO}\cdot\text{CO}\cdot\text{NaO}$ is suggested. In this compound, termed the sodio-cupric carbonate, the copper is electropositive, but has a colour thirty times more intense than the copper in copper sulphate. When excess of normal sodium carbonate is added, the copper becomes electronegative, and no longer reacts with ferrocyanide. The substance then present is what has been termed an α -cupricarbonate, consisting of $\text{Na}_2\text{Cu}(\text{CO}_3)_2$ united with Na_2CO_3 , but in which the copper is joined directly to the carbon atoms, and is in a tetrad condition. It oxidises dextrose, and the constitution suggested represents the presence of a loosely combined oxygen atom explaining such a reaction. Excess of sodium hydroxide decomposes it, but a greater excess dissolves the basic carbonate thrown down, to form a deep violet-blue solution of the β -cupricarbonate, which consists of $\text{Na}_2\text{Cu}(\text{CO}_3)_2$ united with one or two molecules of sodium hydroxide. This, too, oxidises dextrose, and also combines with cellulose. It is stable in the presence of excess of alkali, whereas the α -compound gradually decomposes, either into the crystalline double salt or into malachite. The sodiocupric carbonate decomposes in a similar manner, but generally into malachite.

Incidentally, a new basic sulphate of the composition $15\text{CuO}\cdot\text{SO}_3$ has been obtained.

Addendum.—Since this paper was communicated, some additional evidence in favour of the constitution suggested for the β -cupricarbonate has been obtained, but reasons have also appeared for regarding it as probable that, in the presence of excess of alkali, the introduction of hydroxide into the molecule proceeds a step further than was imagined, the oxygen atom combined with the copper, as well as that combined with the carbon, becoming converted into hydroxyls, and giving a substance containing the cuprate group $\text{Cu}(\text{ONa})(\text{OH})$. It is probably to the presence of this grouping that the substance owes its violet colour and its action on cellulose.

CLX.—*Constitution of Hydroxyazo-compounds. Part II.*
Action of Mercuric Acetate on Benzeneazophenols.

By ALEC DUNCAN MITCHELL and CLARENCE SMITH.

At the present time, the balance of chemical and physical evidence favours the view that hydroxyazo-compounds do not possess a quinonohydrazone structure, and consequently contain a hydroxyl group. The use of phenylcarbimide for the detection of this group suffers from the disadvantage that different temperatures are required for its reaction with para- and with ortho-hydroxyazo-compounds, the former yielding phenylcarbamates in hot benzene (Goldschmidt and Rosell, *Ber.*, 1890, **23**, 489), whereas similar compounds can only be obtained from *o*-hydroxyazo-compounds in the solid form at the ordinary temperature (Goldschmidt and Löw-Beer, *Ber.*, 1905, **38**, 1098). By the use of mercuric acetate, this defect is avoided, and in a previous communication (C. Smith and Mitchell, *Trans.*, 1908, **93**, 842) it has been shown that *o*- and *p*-hydroxyazo-compounds of the benzene series react with this salt in boiling alcohol to form mercuriacetates, the number of mercuriacetate groups introduced being equal to the number of unsubstituted positions ortho to the phenolic hydroxyl group; for reasons therein stated, this behaviour of hydroxyazo-compounds may be regarded as evidence of their azo-structure.

It has been deemed advisable to apply the reaction to hydroxyazo-compounds of the naphthalene series, for here upholders of the quinonohydrazone formula have an argument which is not commonly applicable to the benzenoid compounds, namely, that the condensation of naphthaquinones and aryl hydrazines gives rise to the same substance as is produced by coupling α -naphthols with diazotised primary aromatic amines. Recent work, however, has seriously damaged the validity of this argument for quinonohydrazone structure (Goldschmidt and Löw-Beer, *loc. cit.*; Auwers, *Ber.*, 1907, **40**, 2154; 1908, **41**, 403, 415; Noelting, Grandmougin, and Freimann, *Ber.*, 1909, **42**, 1377); Borsche, in particular, has succeeded in condensing *o*-nitrophenylhydrazine and *p*-benzoquinone to form *o*-nitrobenzeneazophenol, admittedly a hydroxyazo-compound (*Annalen*, 1907, **357**, 171). There seems to be little doubt, therefore, that the so-called naphthaquinonephenylhydrazones are in reality azo-compounds. Their behaviour with mercuric acetate in boiling alcohol supports this view, but the evidence is not as conclusive as could be desired, for although mercuriacetates are formed, except in the cases of benzeneazo- α -naphthol and benzeneazo-

β -naphthol, whenever the hydroxyazo-compound has an unsubstituted position in the ortho- or para-position with respect to the hydroxyl group, mercuriacetates are still formed when there are no such unsubstituted positions. Thus β -benzeneazo- α -naphthol forms a monomercuriacetate as is to be expected, but so also do bisbenzeneazo- α -naphthol, 4-nitro-2-benzeneazo- α -naphthol, and 2-nitro-4-benzeneazo- α -naphthol. Only monomercuriacetates have been obtained even with a large excess of mercuric acetate. The formation of these mercuriacetates, however, was not entirely unexpected, for since it has been shown (C. Smith and Mitchell, *loc. cit.*) that mercuric acetate does not react with the group $\cdot\text{N}_2\cdot\text{C}_6\text{H}_5$, the mercuriacetate complex must have entered the unsubstituted ring of the naphthalene nucleus in the preceding compounds, and probably into position 8, for it is well known that in naphthalene derivatives the peri-position is comparable with the ortho-position in the benzene nucleus (C. Smith, *Trans.*, 1906, **89**, 1505). Since all the preceding hydroxyazo-compounds are derivatives of α -naphthol, the entrance of the mercuriacetate group into position 8 would be in accordance with the rule previously established that the mercuriacetate complex enters the nucleus in the ortho- or para-position with respect to the hydroxyl group. Unfortunately, attempts to settle definitely the orientation of the benzeneazonaphthol mercuriacetates have been unsuccessful, for the replacement of the mercuriacetate complex by any group or atom other than hydrogen has not been accomplished.

The hydroxyazo-compounds obtained by coupling diazotised 2:4:6-tribromoaniline with α -naphthol, 2-nitro- α -naphthol, and 4-nitro- α -naphthol respectively, have been prepared and submitted to the action of mercuric acetate in the hope that the formation of mercuriacetates would prove conclusively that the mercuriacetate group has entered the unsubstituted half of the naphthalene nucleus, but, owing to the extreme insolubility of the three hydroxyazo-compounds in boiling alcohol, the existence of definite mercuriacetates could not be established.

Benzeneazo- β -naphthol does not form a mercuriacetate even when fused with mercuric acetate. Benzeneazo- α -naphthol is oxidised by mercuric acetate, yielding Witt and Dedichen's $\beta\beta$ -dinaphthyl derivative, $\text{C}_6\text{H}_5\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_5(\text{OH})\cdot\text{C}_{10}\text{H}_5(\text{OH})\cdot\text{N}_2\cdot\text{C}_6\text{H}_5$; when the β -position is occupied by a nitro-group, the oxidation is prevented, and 2-nitro-4-benzeneazo- α -naphthol yields a monomercuriacetate in the usual way.

EXPERIMENTAL.

Mercuric Acetate and Benzeneazo- α -naphthol.

A solution containing 14 grams of mercuric acetate in 30 c.c. of warm water and 5 c.c. of glacial acetic acid was added to 10 grams of benzeneazo- α -naphthol dissolved in 700 c.c. of boiling alcohol, and the mixture was heated on the water-bath for six hours. The precipitate, filtered from the hot liquid, was washed with alcohol and with hot water, and repeatedly extracted with boiling dilute acetic acid until the filtrate was free from salts of mercury. The residual chocolate-brown powder, washed finally with alcohol and dried in the steam-oven, weighed 12 grams. It blackened at 227° and melted and decomposed at 248—250°. The substance was extracted with chloroform, whereby a residue of finely divided mercury was left, and by evaporation of the solvent a crystalline substance was obtained, green by reflected and red by transmitted light, which melted and decomposed at 244—246°. It was very sparingly soluble in alcohol or acetic acid and insoluble in aqueous potassium hydroxide, dissolved readily in chloroform or ethyl benzoate, and developed a bluish-purple coloration with concentrated sulphuric acid, changing to indigo-blue on warming. These properties indicated that the substance was Witt and Dedichen's $\beta\beta$ -dinaphthyl oxidation product of benzeneazo- α -naphthol (*Ber.*, 1897, **30**, 2660), and the identity was proved by acetylating the substance by acetic anhydride and anhydrous sodium acetate, and recrystallising the diacetate from toluene. It melted at 263° (Witt and Dedichen's diacetate melts at 264—265°) and gave the following numbers on analysis:

0.1503 gave 0.0595 H₂O and 0.4122 CO₂. C=74.8; H=4.4.

C₃₀H₂₆O₄N₄ requires C=74.7; H=4.5 per cent.

Mercuric Acetate and 2-Nitro-4-benzeneazo- α -naphthol.

The hydroxyazo-compound was prepared by dissolving 3 grams of 2-nitro- α -naphthol and 3 grams of potassium hydroxide in 1500 c.c. of water, cooling to 3—4°, and adding a diazotised solution of 1.5 grams of aniline. After keeping overnight, the red precipitate was collected, washed with water, digested with dilute acetic acid, whereby the red colour changed to orange-yellow, dried, and recrystallised twice from benzene. 2-Nitro-4-benzeneazo- α -naphthol crystallises in orange-red needles, melts at 164°, and develops a bluish-red coloration with concentrated sulphuric acid. It is readily soluble in hot benzene or glacial acetic acid, and

dissolves in warm dilute potassium hydroxide, but is insoluble in a cold concentrated solution :

0.1409 gave 0.3391 CO_2 and 0.0495 H_2O . $\text{C}=65.6$; $\text{H}=3.9$.

0.1651 „, 20.4 c.c. N_2 at 21° and 768 mm. $\text{N}=14.3$.

$\text{C}_{10}\text{H}_{11}\text{O}_3\text{N}_3$ requires $\text{C}=65.5$; $\text{H}=3.7$; $\text{N}=14.3$ per cent.

The *acetyl* derivative was obtained by heating the hydroxyazo-compound for two to three hours with glacial acetic acid, anhydrous sodium acetate, and acetic anhydride, pouring the solution into dilute alcohol, and boiling for a short time until the dark, viscous product had become red and granular. It was collected, washed, dried, and crystallised from glacial acetic acid and twice from benzene, from which it separates in fine, ruby-red prisms melting at 173° :

0.1876 gave 0.4420 CO_2 and 0.0619 H_2O . $\text{C}=64.3$; $\text{H}=3.7$.

$\text{C}_{18}\text{H}_{13}\text{O}_4\text{N}_3$ requires $\text{C}=64.5$; $\text{H}=3.9$ per cent.

To a solution of 1 gram of 2-nitro-4-benzeneazo- α -naphthol in 250 c.c. of boiling alcohol and 5 c.c. of glacial acetic acid was added a solution of 2.5 grams of mercuric acetate in 5 c.c. of warm water, containing a little acetic acid. The clear red solution was heated on the water-bath for six hours, until the precipitate, which had separated, did not increase in quantity. It was filtered hot, washed with alcohol and with boiling water, and finally with hot dilute acetic acid until free from soluble mercury compounds. After being dried in the steam-oven, the mercuriacetate was obtained as a lustrous, reddish-brown, crystalline mass, which blackened at 220° , but was not fused completely at 270° . Being practically insoluble in all solvents, the substance could not be further purified. The analytical data show that the product is a monomercuriacetate :

0.1099 gave 0.1601 CO_2 and 0.0311 H_2O . $\text{C}=39.7$; $\text{H}=3.1$.

0.2110 „, 0.0749 Hg. $\text{Hg}=35.5$.

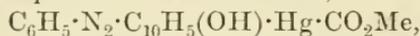
$\text{C}_{18}\text{H}_{13}\text{O}_5\text{N}_3\text{Hg}$ requires $\text{C}=39.2$; $\text{H}=2.4$; $\text{Hg}=36.3$ per cent.

Mercuric Acetate and β -Benzeneazo- α -naphthol.

A solution of 9 grams of mercuric acetate in 25 c.c. of warm water and 5 c.c. of glacial acetic acid was added to 3.5 grams of β -benzeneazo- α -naphthol dissolved in 200 c.c. of hot alcohol containing a little acetic acid. The clear, dark red solution was heated on the water-bath for nine hours, whereby a bulky, red precipitate was formed, and then filtered when cold. By evaporating the filtrate to 50 c.c., a further quantity of the substance was obtained. The combined precipitates were washed with alcohol and with boiling water, and extracted with hot dilute acetic acid until the soluble mercury salts had been removed. The red residue was

finally washed with boiling water and dried in the steam-oven. The yield of the crude mercuriacetate was 6.5 grams or 91.5 per cent. of the theoretical. The purification of the substance presented considerable difficulties, as it is very sparingly soluble in the usual solvents except acetic acid. A pure product can be obtained by the repeated precipitation of a solution in alcoholic sodium hydroxide by acetic acid, but the following process, although attended with great loss of material owing to the fact that the mercuriacetate group is eliminated by boiling glacial acetic acid, was adopted as being the quickest and least inconvenient. Five grams of the finely powdered, crude mercuriacetate were added to 100 c.c. of hot glacial acetic acid, and after a few minutes' boiling the mixture was filtered into 100 c.c. of cold alcohol. The red precipitate was collected, washed thoroughly with alcohol, and dried at 110°; the weight was 3 grams.

β-Benzeneazo-α-naphthol mercuriacetate,



is a brick-red powder, which darkens at 180° and melts with decomposition at 208°:

0.3462 gave 0.5440 CO₂ and 0.0819 H₂O. C=42.8; H=2.6.

0.3198 „ 15.8 c.c. N₂ at 23° and 753 mm. N=5.5.

0.3346 „ 0.1345 Hg. Hg=40.2.

C₁₅H₁₄O₃N₂Hg requires C=42.6; H=2.7; N=5.5;
Hg=39.5 per cent.

The *mercurichloride* is obtained by adding a few c.c. of saturated brine to a solution of 1 gram of the mercuriacetate in hot glacial acetic acid. The red precipitate is collected and washed with acetic acid, alcohol, and with hot water until free from sodium chloride. It is a brick-red powder, which is practically insoluble in the usual solvents; when heated it darkens at 130°, becomes black and semifused at 200°, but is not completely melted at 270°.

Mercuric Acetate and 4-Nitro-2-benzeneazo-α-naphthol.

The hydroxyazo-compound was prepared by adding a diazotised solution of the requisite quantity of aniline hydrochloride to 9.5 grams of 4-nitro-α-naphthol and 11.5 grams of potassium hydroxide dissolved in 200 c.c. of water. The purification was accomplished in the same way as that of the isomeride previously described.

4-Nitro-2-benzeneazo-α-naphthol separates from glacial acetic acid in fine, dark red needles, melts at 180°, and is sparingly soluble in hot alcohol, moderately in glacial acetic acid, and easily in hot benzene. It gives a blood-red coloration with alcoholic potassium hydroxide, and a bluish-red with concentrated sulphuric acid:

0.2007 gave 0.4821 CO₂ and 0.0715 H₂O. C=65.5; H=3.9.

C₁₆H₁₁O₃N₃ requires C=65.5; H=3.7 per cent.

The *acetyl* derivative was obtained by heating 1.3 grams of the substance and 1.5 grams of anhydrous sodium acetate in glacial acetic acid for six hours, pouring the solution into dilute alcohol, collecting the precipitate, and after washing it with alcohol and water, recrystallising it thrice from glacial acetic acid. It separates from this solvent in tufts of orange-red needles, and melts at 208°:

0.1205 gave 0.2837 CO₂ and 0.0420 H₂O. C=64.2; H=3.9.

C₁₈H₁₃O₄N₃ requires C=64.5; H=3.9 per cent.

The *monomercuriacetate* was obtained by adding a solution of 8 grams of mercuric acetate in 30 c.c. of warm water and 10 c.c. of acetic acid to 3.7 grams of 4-nitro-2-benzeneazo-*a*-naphthol dissolved in 1250 c.c. of boiling alcohol. A marked darkening of the colour was observed on mixing the solutions, and a red precipitate soon began to separate. After being heated on the water-bath for twelve hours, the liquid was filtered hot, and the precipitate was washed with alcohol, water, and boiling dilute acetic acid until the substance was free from soluble mercury compounds. After being dried at 110° the product was extracted twice with 200 c.c. of boiling benzene to remove any unchanged hydroxyazo-compound. The residual mercuriacetate was a red substance with the appearance of amorphous phosphorus. It melted and decomposed at 221—222°, and was practically insoluble in the ordinary solvents. It could not be obtained quite pure, but the analysis left no doubt that the substance was a monomercuriacetate:

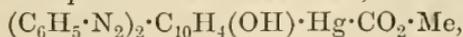
0.2837 gave 0.0995 Hg. Hg=35.1.

C₁₈H₁₃O₅N₃Hg requires Hg=36.3 per cent.

Mercuric Acetate and Bisbenzeneazo-a-naphthol.

Seven grams of the disazo-compound dissolved in 400 c.c. of hot alcohol were heated on the water-bath for six hours with a solution of 13 grams of mercuric acetate in water containing a little acetic acid. The precipitate was collected, washed thoroughly with hot dilute acetic acid, with hot alcohol, and finally with hot benzene to remove any unchanged bisbenzeneazo-*a*-naphthol. The dry crude product, weighing 13.5 grams, was crystallised from phenol containing a little alcohol. It was usually obtained as a dark brownish-purple, crystalline powder, but on one occasion the mercuriacetate separated in lustrous, black needles with a bronze lustre.

Bisbenzeneazo-a-naphthol mercuriacetate,



softens at 218°, and melts and decomposes at 235—238°. It shows

the usual properties of a mercuriacetate, being almost or quite insoluble in the common solvents, and having the mercuriacetate group eliminated by acids; it gives with concentrated sulphuric acid a reddish-violet coloration similar to that given by the original hydroxyazo-compound:

0.2203 gave 0.3840 CO_2 and 0.0582 H_2O . $\text{C}=47.5$; $\text{H}=2.9$.

$\text{C}_{24}\text{H}_{15}\text{O}_3\text{N}_4\text{Hg}$ requires $\text{C}=47.2$; $\text{H}=2.9$ per cent.

2': 4': 6'-Tribromo-4-nitro-2-benzeneazo- α -naphthol.

A solution of 8 grams of 2:4:6-tribromoaniline in 45 c.c. of alcohol and 30 c.c. of concentrated nitric acid was diazotised at 0° by cold nitrous fumes, and added slowly to 3 grams of 4-nitro- α -naphthol and 30 grams of potassium hydroxide in 1200 c.c. of water. After remaining overnight, the precipitate was collected, washed with alcohol, digested with hot dilute acetic acid, washed with water, and dried in the steam-oven. By repeated solution in hot nitrobenzene and precipitation by alcohol, 3.5 grams of a brilliant orange-red substance were obtained, which melted at $213-214^\circ$; the hydroxyazo-compound was finally recrystallised from boiling amyl alcohol, from which it separates in orange-red needles of the same melting point:

0.2388 gave 0.2534 AgBr . $\text{Br}=45.2$.

$\text{C}_{16}\text{H}_5\text{O}_3\text{N}_3\text{Br}_3$ requires $\text{Br}=45.2$ per cent.

2': 4': 6'-Tribromo-4-nitro-2-benzeneazo- α -naphthol is very sparingly soluble in alcohol, benzene, and other low boiling solvents, but dissolves readily in hot amyl alcohol, nitrobenzene, or ethyl benzoate; it develops, with concentrated sulphuric acid, a cherry-red coloration with a violet shade, and forms an *acetyl* compound which melts at 186° .

2': 4': 6'-Tribromo-2-nitro-4-benzeneazo- α -naphthol.

A suspension of 15 grams of 2:4:6-tribromoaniline in 80 c.c. of alcohol and 15 c.c. of concentrated nitric acid was diazotised at 0° by cold nitrous fumes, and the solution added to 5 grams of 2-nitro- α -naphthol and 5 grams of potassium hydroxide in 3 litres of water, a solution of an additional 15 grams of potassium hydroxide being added in small quantities from time to time in order to keep the mixture alkaline. After remaining overnight, the precipitate was collected, washed with water, digested with hot dilute acetic acid, and finally boiled with alcohol to remove a little 2-nitro- α -naphthol. The crude product, weighing 13.3 grams, was twice recrystallised from nitrobenzene, washed with alcohol, and dried.

2': 4': 6'-Tribromo-2-nitro-4-benzeneazo- α -naphthol crystallises in orange-yellow plates and melts at 216°; it is less soluble than the preceding isomeride, and gives an intense violet-red coloration with concentrated sulphuric acid:

0.2225 gave 0.2353 AgBr. Br=45.0.

$C_{16}H_8O_3N_3Br_3$ requires Br=45.2 per cent.

Bis-2': 4': 6'-tribromobenzeneazo- α -naphthol.

The production of this compound from α -naphthol and diazotised 2: 4: 6-tribromoaniline (2 mols.) was accomplished as in the preceding preparation. The substance was purified by repeated crystallisation from benzene, whereby it was obtained as a dark maroon powder, which melted at 249—253° and gave a blue coloration with concentrated sulphuric acid:

0.1984 gave 0.2685 AgBr. Br=57.6.

$C_{22}H_{10}ON_4Br_6$ requires Br=58.1 per cent.

In conclusion, the authors desire to express their indebtedness to the Research Fund Committee of the Chemical Society for a grant in aid of this investigation.

EAST LONDON COLLEGE.

CLXI.—*The Amygdalins. Part I.*

By J. WALLACE WALKER and VERNON K. KRIEBLE.

IN a previous communication by one of us (Walker, *Trans.*, 1903, 83, 472) it was demonstrated that *l*-amygdalin is converted rapidly at the ordinary temperature by a very small quantity of an alkaline solution into a much more soluble substance, which yields on hydrolysis by concentrated hydrochloric acid, not *l*-mandelic, but *r*-mandelic acid. Although the new material was termed provisionally *r*-amygdalin, proof was wanting that it is even a homogeneous substance, since it could not be obtained crystalline. The author stated that it was still under examination, and consequently was much surprised to find Dakin (*Trans.*, 1904, 85, 1512) claiming to have isolated it in crystalline form. It may be well therefore to state here that its study had been continued; that a very soluble, crystalline substance had already been isolated from aqueous or aqueous-alcoholic solution, which proved not to be *r*-amygdalin, since it yielded mandelic acid possessed of a high levorotation; that this

substance yielded on fractional crystallisation ordinary or *l*-amygdalin; that the mother liquor on acid hydrolysis gave a large preponderance of *d*-mandelic acid; that the racemised solution, as was to be anticipated, gave benzaldehyde and hydrocyanic acid with emulsin; and that the mandelic acid obtained from the racemised solution was in no case absolutely inactive, but always contained a small excess of the dextro-variety. There were, however, a number of questions which for a long time defied the attempts made to elucidate them, and some of these we have only as yet been able to answer in part satisfactorily.

Regarding the nomenclature to be adopted, we shall employ that indicated in the former communication, considering it preferable to the *iso*-amygdalin of Dakin or the *neo*-amygdalin of Tutin (Trans., 1909, 95, 663), and designate ordinary amygdalin as *l*-amygdalin, since it yields *l*-mandelic acid and the isomeride which only differs from it in yielding *d*-mandelic acid on hydrolysis as *d*-amygdalin, leaving to their discoverer the task of assigning names to the similar compounds which contain the different varieties of *d*- and *l*-glucose.

In the former communication the simplest assumption was made regarding the nature of the change induced in the molecule of amygdalin by alkalis, namely, that it consists only in the racemisation of the mandelic asymmetric carbon atom, although further change, for example, that of a β - into an α -glucoside, was not excluded. We have reason now to conclude that a partial change of that nature does occur during racemisation, and to a much greater extent on protracted concentration of the solution, especially in presence of barium carbonate. This of course complicates the problem, and renders it difficult to decide whether the small excess of dextro-acid which is invariably found on hydrolysis represents a displacement of the equilibrium in the transformation *levo* \rightleftharpoons *dextro* beyond the middle point. We have proved, however, that the rotation of the racemised solution is independent of the nature and of the concentration of the alkali, and that the equilibrium-point is independent of temperature and of the concentration of the amygdalin. In studying the fractional crystallisation of the racemised solution, we find that the less soluble fraction yields on hydrolysis mandelic acid containing 78 per cent. of the *levo*-variety, and that the more soluble fraction obtained by suitable means from the mother liquor gives mandelic acid containing 75 per cent. of the dextro-variety. These figures point to the presence of the respective compounds (*3l* + *d*)- and (*3d* + *l*)-amygdalin, but their rotations are not quite in conformity with this supposition, nor is the behaviour of the second, when subjected to the action of emulsin, such as we would expect from a compound having the composition (*3d* + *l*)-amygdalin. We are driven therefore to the conclusion that

the second compound at least does not contain the substance which we have termed *d*-amygdalin, and that the change induced in *l*-amygdalin by alkalis is of a much more complicated nature than has been hitherto assumed.

EXPERIMENTAL.

The material employed throughout this investigation was Kahlbaum's preparation. Analyses showed that it possesses the formula



and that when it is allowed to crystallise from aqueous solution the air-dried material contains 3 molecules of water of crystallisation. Its specific rotation, and that of its racemised solution, were determined at different temperatures and concentrations. The results contained in the following tables, as well as all that follow, refer to the anhydrous substance.

TABLE I.

l-Amygdalin.

<i>t</i> .	$[\alpha]_D$.
<i>c</i> = 18.54.	
20.5°	-38.0°
29.0	37.1
42.0	35.8
<i>c</i> = 9.27.	
8.0°	41.6°
16.0	40.1
20.0	39.3
25.0	38.8
28.5	38.3
40.0	36.8
48.0	35.8

TABLE II.

r-Amygdalin

<i>t</i> .	$[\alpha]_D$.
<i>c</i> = 17.657.	
13.0°	-54.4
40.0	50.8
<i>c</i> = 8.9.	
23.0°	-52.8°
38.0	51.0
<i>c</i> = 6.39.	
26.0°	-52.4°
<i>c</i> = 4.414.	
23.0°	-52.6°

TABLE III.

l-Amygdalin. *t* = 28.5°.

<i>c</i> .	$[\alpha]_D$.	<i>c</i> .	$[\alpha]$.
18.54	-37.1°	4.472	-39.0°
9.27	38.3	2.236	39.4
6.71	37.8		

These observations show a large and approximately equal variation with temperature for both substances. The variation with concentration is much smaller in the case of *l*-amygdalin and negligible for *r*-amygdalin.

The Equilibrium between Laevo- and Dextro-amygdalin.—Since the two forms are not optical antipodes, there seems no reason to expect

that the equilibrium point should lie exactly midway between the two, and even in the former communication it was noted, as has been confirmed by Dakin, that after complete hydrolysis of the racemised solution with hydrochloric acid, the ethereal extract did possess a slight activity, pointing to the production of a slight excess of *d*-amygdalin, although Liebig and Wöhler's amygdalinic acid gave quite inactive mandelic acid. This has been fully confirmed in a large number of subsequent experiments in which the hydrolysis was performed both at the ordinary temperature and on the boiling-water bath. If the equilibrium point, however, were not situated midway between the two extremes, it is probable that by varying the conditions of racemisation there would be a consequent displacement of the equilibrium point. Of the four variable factors which may influence the equilibrium point, namely, temperature, concentration of the amygdalin, and the nature and concentration of the alkali, the last two will be excluded if it can be shown that the reaction is purely catalytic, and this was roughly done in the previous communication. It has been considered advisable therefore to obtain more accurate proof of the catalytic nature of the change. The alkali, however, may also slowly hydrolyse both varieties of amygdalin to their respective amygdalinic acids, and, if it does so at unequal rates, but with a velocity at all comparable to that of racemisation, the dextro-variety, if more rapidly hydrolysed by alkalis, as Dakin has shown (*loc. cit.*), than it is by acids, would be continuously produced from the levo-. It was therefore considered necessary to examine also the velocity of the change of amygdalin into amygdalinic acid in alkaline solution, although the facts recorded formerly, namely, that no ammonia could be detected after racemisation, and that amygdalinic acid yields *r*-amygdalinic acid, were strong evidence that alkaline hydrolysis is not responsible for the excess of mandelic acid obtained. The velocity of racemisation was observed in the 2-dcm. tube at 16°. The first three solutions were prepared by adding 1 c.c. of the alkaline solution to 25 c.c. of a 10 per cent. solution of recrystallised *l*-amygdalin, the fourth by adding 1 c.c. of alkali to 50 c.c.

TABLE IV.

<i>Catalyst, Barium Hydroxide. 1 c.c. added to 25 c.c.</i>			
{ Observed rotation.	Time (in minutes).	<i>A - α.</i>	<i>K.</i>
-6.86° (calculated)	0	2.24	—
7.72	2	1.38	0.105
8.31	4	0.79	0.113
8.65	6	0.45	0.116
8.88	9	0.22	0.112
9.09	14	0.10	0.168

TABLE IV (continued).

Catalyst, Potassium Hydroxide. 1 c.c. added to 25 c.c.

Observed rotation.	Time (in minutes).	<i>A</i> - <i>x</i> .	<i>K</i> .
-6.86°	0	2.24	—
7.75	2	1.35	0.110
8.28	4	0.82	0.109
8.59	6	0.51	0.107
8.85	9	0.25	0.106
9.03	14	0.07	0.108
9.11	20	—	—
9.11	30	—	—

Catalyst, Lithium Hydroxide. 1 c.c. added to 25 c.c.

-6.86°	0	2.24	—
7.72	2	1.38	0.105
8.25	4	0.85	0.105
8.63	6	0.47	0.113
8.86	9	0.24	0.108
9.08	14	0.02	0.146
9.10	20	—	—

Catalyst, Lithium Hydroxide. 1 c.c. added to 50 c.c.

-7.00° (calculated)	0	2.24	—
7.43	2	1.81	0.046
7.88	4	1.35	0.054
8.21	6	1.03	0.056
8.54	9	0.70	0.057
8.88	14	0.36	0.056
9.11	22	0.13	0.073
9.24	33	—	—
9.25	58	—	—

The mean total change of rotation is 2.24°, and as the slight deviations are well within the limit of experimental error this may be taken as a measure of the total chemical action. The values of *K*, calculated by means of the unimolecular equation, are seen to be in satisfactory agreement in experiments I, II, and III, whilst that in experiment IV is just half value. Consequently all the alkalis examined racemise amygdalin with the same velocity in equivalent solutions, and when their concentration is halved the velocity of their action is also reduced to half. These are the criteria for a catalytic action. It is further important to note that, within the limits studied, the concentration of the alkali has no influence on the end point. As these limits are, however, somewhat narrow, it was considered advisable to extend them. In the following experiments, which were done at 25°, the volumes of water and barium hydroxide (1 c.c. = 0.0122 gram

Ba(OH)₂ specified were added to 20 c.c. of a 10 per cent. solution of *l*-amygdalin and the final rotation examined in the 1-dem. tube :

C.c. water.	C.c. baryta.	Final value of α_D .
8	1	-3.35°
4	5	3.35
3	6	3.35
1	8	3.35

It is obvious that the concentration of the alkali is without influence. At 25° the velocity of racemisation was so great that the change was almost complete by the time that the first reading could be taken.

The velocity of hydrolysis of amygdalin to amygdalinic acid was also examined polarimetrically, using a solution of sodium hydroxide containing 0.1 gram-molecule in 50 c.c. For this purpose 10 grams of recrystallised *l*-amygdalin were dissolved in water containing five equivalents of sodium hydroxide and diluted to 50 c.c., the change of rotation being followed at 20° in the 2-dem. tube :

TABLE V.

Time.	α_D .	$A - x$.	K .
0	(-18.80°)	5.76	—
14	19.40	5.16	0.00012
27	20.00	4.56	0.00013
77	21.40	3.16	0.00012
147	22.30	2.26	0.00010
297	23.54	1.02	0.00010
387	23.80	0.76	0.00009
1360	24.56	0.00	—

The initial reading, namely, -18.80°, obtained by plotting the subsequent values and extrapolating, corresponds with a specific rotation for anhydrous *r*-amygdalin of $[\alpha]_D$ -52.5°, which is identical with that given in Table II, showing that the equilibrium point of the reaction is the same even at this concentration of alkali as in the very dilute. The values of K , calculated from the equation for a bimolecular reaction, are in good agreement, and it is evident that the time taken is about 1000 times as long as that for racemisation, even although the alkali is now more than 300 times stronger. It is certain therefore that hydrolysis plays no part during racemisation and is not responsible for any excess of *d*-mandelic acid obtained on acid hydrolysis. Concurrent experiments to be described later on the fractional crystallisation of *r*-amygdalin had led us to look upon the dextro-variety as an extremely soluble substance compared with its *l*-isomeride, which could be isolated by fractional crystallisation from the racemised solution, and it seemed natural to associate the over-production of the dextro-variety with its great solubility. If this were the

case we should expect to find that, by racemising in a very concentrated solution, a greater excess of the dextro-variety would be produced. Consequently a series of experiments were made in which the concentration of the amygdalin varied from $c=17.657$ to 4.414 and the rotations of the resulting racemised solutions were observed. The results are contained in Table II. As already stated they show that the specific rotation of the racemised solution is independent of the concentration of the amygdalin. Even more concentrated solutions of *r*-amygdalin than these were produced by adding a small quantity of baryta solution to solid amygdalin. After acid hydrolysis and extraction with ether the mandelic acid obtained had always about the same specific rotation, namely, $+16^\circ$, indicating therefore about 15 per cent. excess of dextro-acid. A somewhat higher result was obtained by the polarimetric study of the hydrolysis of *r*-amygdalin. The concentration of anhydrous material was 9.442 and the hydrolyst, hydrochloric acid ($D=1.1$). The change of rotation was followed in the 2-dcm. tube at 40° .

TABLE VI.

Time (in hours).	α_D .	Time (in hours).	α_D .
0.5	-19.76°	22	+3.64°
1.5	19.7	41	12.22
2.75	18.64	66	16.74
5.75	15.48	89	18.70
17.0	-0.88	114	20.16

There was no further change on prolonged heating at the same temperature. If inactive mandelic acid and dextrose be the sole products of hydrolysis, the final rotation of the solution should be $+15.8^\circ$. The excess of dextrorotation observed is $+4.4^\circ$, which corresponds with 21 per cent. excess of *d*-mandelic acid, since the specific rotation of the latter is $+168^\circ$ when dissolved in that strength of hydrochloric acid. We have not yet been able to account for the difference in the results obtained by the two methods except on the assumption that the dextrose has also undergone some change.

The last factor which can influence the racemisation and produce excess of the dextro-variety is temperature; consequently, in order to investigate this point, two experiments were performed, one at 50° , the other at 100° , the amygdalin being racemised in each case with 10 c.c. of the baryta solution. After complete acid hydrolysis they were extracted with ether and a specific rotation taken of the dry acids. It was found in both cases to be 16° . Consequently temperature has no influence on the equilibrium point during racemisation. These facts, all taken in conjunction, point to the conclusion that there is actually a racemic compound in solution, and that the production of an excess

of *d*-mandelic acid from it is due to an inequality in the rates of hydrolysis of the two varieties by acid, accompanied by a slow racemisation in that medium also. The experiments now to be described on the fractional crystallisation of the racemised solution indicate, however, that the material contained in it may not be of such a simple nature.

The Partial Resolution of γ -Amygdalin.—This had been effected before the last communication was published, but, owing to its incompleteness, it was reserved for further study and only the statement made that the racemic compound could not be obtained crystalline. Successive crops of crystals had been obtained, however, either from aqueous or alcoholic solution, but these, although showing a far greater solubility in water than *l*-amygdalin, were not constant in specific rotation, nor had the latter nearly so high a value as that of the racemised solution. Further, it was frequently found impossible to induce crystallisation at all, but the syrup obtained on evaporation would dry up to a glassy mass. It was found, however, that when a crop of very soluble crystals was obtained, it yielded on recrystallisation almost pure *l*-amygdalin, and that, after a large amount of gummy material had been precipitated from the alcoholic mother liquor by the addition of ether, the residue left on the evaporation of the ether yielded, when hydrolysed with hydrochloric acid, a sample of mandelic acid melting at 120–125° and showing a specific rotation of +99°. A partial separation had therefore been effected by fractional crystallisation and precipitation. In a very recent communication Tutin (Trans., 1909, 95, 663) has shown that this may also be effected in the case of hepta-acetyl- γ -amygdalin; but here also the separation is far from quantitative, for Tutin only obtained 9 grams of crystalline material from 20 grams of γ -amygdalin instead of the theoretical 16.5 grams, and even that was evidently far from pure hepta-acetyl-*d*-amygdalin. This is exactly on a parallel with what we have observed in our very numerous experiments on the fractional crystallisation of γ -amygdalin. We always obtain a considerable amount of uncrystallisable gum which yields excess of *d*-mandelic acid on acid hydrolysis. At first it seemed probable that this is due to some *l*-amygdalin separating with the less soluble fraction, thus leaving an excess of the non-crystallisable *d*-amygdalin in the mother liquor; but subsequent experiments involving a study of the action of emulsin on the different varieties, and of the electrical resistances of the solutions before and after evaporation, have led us to conclude that they may, according to the treatment which they have undergone, contain 50 per cent. or even more of something which is not one of the amygdalins. Our reasons for concluding that it may to that extent have undergone an isomeric change will appear in the description of a few of our experiments

bearing on that point. Assuming for the present that the solution contains only *l*- and *d*-amygdalin in equivalent amounts, it is evident from the specific rotations of *l*- and *r*-amygdalin, namely, -39.3° and -53° in 10 per cent. solution at 20° , that the specific rotation of *d*-amygdalin must be -66.7° under the same conditions. We should have therefore for $(3l+d)$ -amygdalin $[\alpha]_D - 46.2^\circ$ and for $(3d+l)$ -amygdalin $[\alpha]_D - 59.9^\circ$. The best method yet devised for conducting the fractional crystallisation is as follows. After racemising 200 grams by baryta, the solution was saturated by carbon dioxide and the barium carbonate removed by filtration. The filtrate was evaporated to a syrup, and dissolved in a litre of 95 per cent. alcohol. After being kept at 0° for several hours, 80 grams of crystalline material were obtained. On drying over phosphoric oxide in a vacuum it lost weight equivalent to two molecules of water of crystallisation. The specific rotation of the anhydrous substance was $c=9.27$, $t=28.5^\circ$, $\alpha_D - 8.65^\circ$; hence $[\alpha]_D - 46.6^\circ$. At 20° , therefore, its specific rotation must be -47.7° , assuming that the temperature coefficient is the same for this substance as for the other two. This value is in fairly close agreement with that calculated above for a substance possessing the composition of $(3l+d)$ -amygdalin. Ten grams of it were hydrolysed with hydrochloric acid (D 1.118), and the mandelic acid, after extraction with ether, was converted into the barium salt (3.7 grams). Analysis showed that it was almost pure barium mandelate. When dissolved in water and diluted to 50 c.c., it showed a rotation of $\alpha_D - 6.8^\circ$ at 20° in the 2-dcm. tube. The specific rotation of pure barium *l*-mandelate was found to be $[\alpha]_D - 80.9^\circ$ under the same conditions; hence the concentration of lævo-salt in excess in the above solution is $c = 6.8 \times 100/80.9 \times 2 = 4.2$. Therefore 3.7 grams contain 2.1 grams of lævo-salt in excess and 1.6 grams of racemic salt or a total of 78.4 per cent. of the lævo-compound. That this crystalline material is mainly a definite compound and not a mixture of *l*- and *r*-amygdalin was evident from the extreme ease with which it dissolved in water. From the result of its hydrolysis, however, it evidently contained a small quantity of free *l*-amygdalin. After being twice crystallised from water, it gave, on acid hydrolysis, a sample of mandelic acid, showing the specific rotation $[\alpha]_D - 142.5^\circ$. It contained, therefore, less than 8 per cent. of *d*-mandelic acid. The original mother liquor from the 200 grams of amygdalin was concentrated to a syrup and then extracted with 300 c.c. of a boiling mixture containing one part of alcohol to three of ethyl acetate. The residue, obtained after evaporation of the solvent, was dried over sulphuric acid until constant in weight. It weighed 35 grams. As it was non-crystalline, we had no criterion that it was a chemical individual. It was therefore re-dissolved in 350 c.c. absolute alcohol, and this solution kept for some time at about -18° . The crystalline

material (10 grams) which separated was rapidly dried and transferred at once to weighing bottles. These precautions are necessary, for at a slightly higher temperature the crystals liquefy. The material in the weighing bottles rapidly melted, and was kept in a vacuum over sulphuric acid until constant in weight. In this way it lost 35 per cent. in weight, corresponding with 5.35 molecules of alcohol. The material dried over sulphuric acid was employed for determining its specific rotation with the following results: $c=5.9$, $t=29^\circ$, $l=1$ -dm., $\alpha_D - 3.25^\circ$; hence $[\alpha]_D - 55.1^\circ$. At 20° , therefore, its rotation will be about -56° . Ten grams of it, when hydrolysed as above, yielded 4.35 grams of barium mandelate, showing the rotation $c=8.7$, $l=2$ -dm., $\alpha_D + 7.25^\circ$. It therefore contained 75.7 per cent. of dextro-salt. Its rotation, however, does not correspond with the value calculated for $(3d+l)$ -amygdalin. The alcoholic solution from which this modification of amygdalin was obtained yielded further crops of the same material on evaporation.

Action of Emulsin on the Amygdalins.—When a solution of emulsin was added to the racemised solution of amygdalin and the mixture kept for several hours at 40° in a closed flask, it acquired a strong odour of oil of bitter almonds. This was also observed by Dakin (*loc. cit.*), but this qualitative observation is of no further value than to afford proof that the solution still contains *l*-amygdalin. A series of comparative experiments has therefore been conducted quantitatively to determine the action of emulsin on these different substances. The emulsin employed was Kahlbaum's preparation. After the solutions had been heated at 40 — 45° for twenty-four hours, the liberated hydrocyanic acid was estimated by the method described by Auld (*Trans.*, 1908, 93, 1277) and the dextrose by Fehling's solution. The former we found far from satisfactory, as the end point is by no means sharp, although accurate enough for comparative results. In the following table are given the averages of several determinations.

TABLE VII.

	0.2833 gram of substance required of N/50-iodine (in c.c.).	1.89 grams yielded of dextrose (in grams).
<i>l</i> -Amygdalin	52.3	1.5
<i>r</i> -Amygdalin	26.0	1.19
$(3d+l)$ -Amygdalin (?)	18.6	—

Since the values of iodine for the first two are very nearly in the ratio 2 : 1, the conclusion seemed obvious that emulsin only liberates hydrocyanic acid from the *l*-amygdalin present, and, as the amounts of dextrose are approximately in the ratio 4 : 3, that it is only capable of removing one molecule of dextrose from the supposed *d*-amygdalin.

If it contains *d*-amygdalin, the second substance ought to yield, on partial hydrolysis by emulsin, *d*-mandelonitrile glucoside. But Caldwell and Courtauld (*Trans.*, 1907, 91, 673) have pointed out that the substance sambunigrin, isolated by Bourquelot and Danjou (*Compt. rend.*, 1905, 141, 598) from elder leaves, must be *d*-mandelonitrile glucoside; consequently our solution ought to contain sambunigrin. That it does not contain that substance, however, was proved by the fact that emulsin is unable to hydrolyse it, for no further change took place on heating at 40° for forty-eight hours longer. We therefore attempted to isolate the new substance by concentrating to a syrup and extracting with ethyl acetate, but the residue left after evaporating the ethyl acetate did not crystallise even after a long period. This result led us to conclude that some further change than simple racemisation had taken place in the amygdalin molecule; accordingly, another set of comparative experiments was made to determine whether it is contemporaneous with, or subsequent to, racemisation. The concentration of the emulsin was lower in these, so that it is improbable that hydrolysis was carried as far as in the previous experiments.

0.3 gram substance required of *N*/50-iodine :

(1) Racemised without heating	42 c.c.
(2) Racemised and dried for 4 hours on the water-bath	21 ,,

These results suggested an explanation of several difficulties, showing as they do that a profound change takes place when the solution is evaporated to dryness. They indicated a reason for the large quantities of uncrystallisable material which we frequently obtained, and pointed to a probable change in the rotatory power of the racemised solution by protracted evaporation. Our early determinations of this constant had shown considerable inexplicable divergences from each other. There are three possible directions in which the structure of the molecule may be affected by heating. It may suffer an isomeric change in one or both of its dextrose radicles, it may lose one dextrose radicle by hydrolysis, or it may be hydrolysed to the ammonium salt of amygdalinic acid. That dextrose was not liberated was shown by testing the evaporated material with Fehling's solution. The result was negative. As none of the ordinary methods of testing for the presence of an ammonium salt recommended themselves in this case, we finally decided to take the decrease in electrical resistance of the solution as a measure of the amount of such hydrolysis, and, at the same time, to measure the change in optical power. In the cell which we employed the ordinary distilled water of the laboratory had a resistance of 16,000 ohms at 19°, whilst a 5 per cent. solution of

the material employed, namely, $C_{20}H_{27}O_{11}N, 3H_2O$, had a resistance of 2,444 ohms.

For the purpose of comparison 5 grams of the same sample were boiled with excess of baryta until all the ammonia was expelled; then carbon dioxide and ammonia were passed into the solution to precipitate all the barium as carbonate and give a solution of ammonium amygdalinate. This was thoroughly boiled to expel dissolved gases, diluted to 100 c.c., and found to be neutral in reaction and free from barium. Its specific rotation was $[\alpha]_D^{20} - 72^\circ$, and its resistance 15 ohms. In the following three experiments 2.5 grams of *l*-amygdalin were racemised with baryta, and, after precipitation of the latter by carbon dioxide, were evaporated on the water-bath for the times specified. They were then diluted to 50 c.c., filtered, and their electrical resistances and specific rotations measured. In the first experiment 10 c.c. were hydrolysed by emulsin for twenty-four hours, and the liberated hydrocyanic acid was titrated with *N*/50-iodine.

TABLE VIII.

Time (in hours).	Ohms.	$[\alpha]_D$ (anhydrous).	C.c. <i>N</i> /50-iodine.
8	148	- 61.0°	24
4	200	60.6	—
2	273	52.7	—

If we assume as an approximation that the resistance of a solution of ammonium amygdalinate is proportional to its concentration, the 5 per cent. solution of that salt would evidently require to be diluted to nearly ten times its volume to show a resistance equal to the first of these. That is to say, 10 per cent. at most of the amygdalin has been hydrolysed. When we examine the specific rotations, however, we find that $61 - 52/72 - 52 = 9/20$ ths, or 45 per cent. has been changed, assuming hydrolysis to be the cause. In the third experiment, conditions are reversed, for there practically no change has occurred in the optical properties of the solution, although its resistance would indicate 5 per cent. of hydrolysis. Finally, without any assumption as to the nature of the change, when the amount of hydrocyanic acid liberated is compared with that produced under similar conditions from a racemised solution which has not been heated, we find that 66 per cent. has been changed, for such a solution required 70 c.c. *N*/50-iodine. We must conclude, therefore, that the chief change which takes place on protracted heating is not a hydrolytic one, but consists in some intramolecular transformation, a new isomeride of amygdalin being produced which probably bears to amygdalin the relationship of an α -glucoside to a β -glucoside. Our experiments are, however, not yet

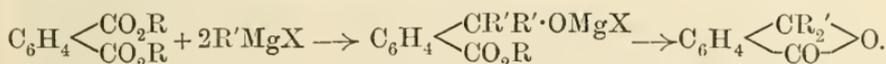
decisive as to whether the freshly racemised solution contains *d*-amygdalin or not, but we are continuing the study of the subject.

MACDONALD CHEMISTRY AND MINING BUILDING,
MCGILL UNIVERSITY.

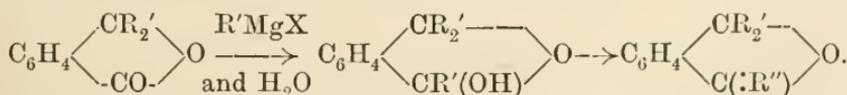
CLXII.—*The Action of the Grignard Reagent on Phthalic Esters.*

By YŪJI SHIBATA.

THE action of the Grignard reagent on succinic esters results according to A. Valeur (*Bull. Soc. chim.*, 1903, [iii], 29, 683) and W. Dilthey and E. Last (*Ber.*, 1904, 37, 2640) in the production of tetra-alkylbutandiols, $\text{OH}\cdot\text{CRR}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CRR}\cdot\text{OH}$. I have recently studied the action of the same reagents on phthalic esters, which are known to have an analogous constitution to succinic esters, expecting that, in this case also, glycols would be produced. It was found, however, that this is by no means the case, derivatives of phthalide being produced according to the following scheme :



Generally, however, the reaction proceeds one step further, the ketone group contained in dialkylphthalide, thus formed, combining with another molecule of the Grignard reagent, and the resulting compound decomposing in contact with water and producing the anhydro-compound,* as shown below :



The resulting compound is thus a derivative of phthalan (*o*-xylylene oxide),



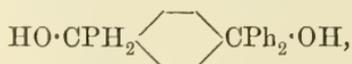
(A. Ludwig, *Ber.*, 1907, 40, 3062). The intermediate carbinol could not be isolated.

* It appears likely that the dehydration is due to the action of the excess of the Grignard reagent employed (compare F. W. Kay and W. H. Perkin, jun., *Trans.*, 1906, 89, 848, etc.).

This difference in the action of the Grignard reagent on the esters of succinic and phthalic acids may be easily explained by taking into consideration the position of the carboxyl groups in the molecule of the two acids.

As first pointed out by H. G. Bethmann (*Zeitsch. physikal. Chem.*, 1890, 5, 409), certain properties of succinic acid correspond with the following space formula, with its two carboxyl groups in the *trans*-position, and the ease with which succinic esters react with four molecular proportions of the Grignard reagent and produce glycols can be readily explained by adopting the same formula, the two carboxyl groups in the *trans*-position having no space influence on the course of the reaction. In the case of phthalic acid, however, only one ester group reacts with two molecular proportions of the Grignard reagent, as already pointed out, and phthalide is formed as the intermediate product. This must be considered as due to the steric hindrance, or, in other words, to the effect of the *cis*-position of the two carboxyl groups in phthalic acid.

On the other hand, F. Ullmann and C. Schlaepfer (*Ber.*, 1904, 37, 2003) obtained tetraphenyl-*p*-xylylene glycol,



by the action of magnesium phenyl bromide on dimethyl terephthalate, the reaction being evidently quite analogous to that which occurs in the case of succinic esters. It thus appears very probable that the two carboxyl groups in terephthalic acid are in the *trans*-position.

These considerations enable us to discuss a little more fully than hitherto the different space formulæ of benzene proposed from time to time. The following may be regarded as their representatives :

FIG. I.

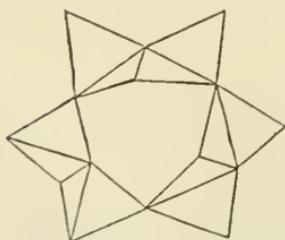
Graebe (*Ber.*, 1902, 35, 526).

FIG. II.

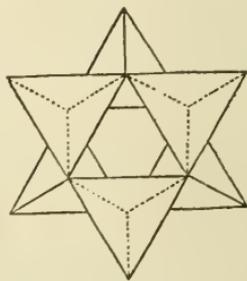
Sachse (*Ber.*, 1888, 21, 2530).

FIG. III.

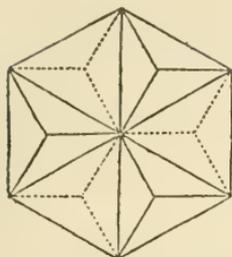
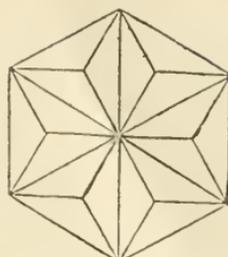


FIG. IV.

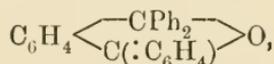


Vaubel (*J. pr. Chem.*, 1891, [ii], 44, 137). Baeyer (*Annalen*, 1888, 245, 123).
Erlenmeyer, jun. (*ibid.*, 1901, 316, 57).

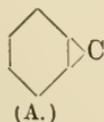
Of these, neither III nor IV appear to be in agreement with the facts mentioned above, for, according to III (which is constructed by laying six tetrahedra alternately above and below the plane formed by their bases), phthalic esters, in reacting with the Grignard reagent, should, like terephthalic and succinic esters, also give glycols, which is not found to be the case, whilst in IV (which is constructed by laying six tetrahedra on a plane hexagon), although the distance between the para-positions is double that between the ortho-positions, the two carboxyl groups in terephthalic acid have the same orientation, and must therefore, to a certain extent, have a hindering influence on each other in carrying out the Grignard reaction. This again is not the case.

On the other hand, both I and II satisfy the main condition that the two carboxyl groups in phthalic acid are in the *cis*-position, whilst those in terephthalic acid are in the *trans*-position.

The choice between these two is not so easy to make. But, as will be shown hereafter, I have obtained I : 1-diphenyl-3-phenylenephthalan,



by the action of magnesium phenyl bromide on diethyl phthalate, this compound being, no doubt, produced through the intermediate formation of the alcohol, $\text{C}_6\text{H}_4 \left\langle \begin{array}{c} \text{CPh}_2 \\ \text{CPh}(\text{OH}) \end{array} \right\rangle \text{O}$, as already indicated above in a general way, the alcohol losing water from the group $\text{:CPh}\cdot\text{OH}$. Now, there are three possible ways in which water may be separated from this group, according as the condensation occurs in the ortho-, the meta-, or the para-position, thus producing one or other of the following three double rings :



Referring to formulæ I and III, which are to be preferred to

formulae III and IV, as already indicated above, we shall easily find that formula II, proposed by Sachse, which is constructed in such a way that the six tetrahedra are all rigidly combined with one another, and in which the distance between the two free solid angles of any two adjacent tetrahedra is too great for a third tetrahedron of the same size to fit in, cannot account for the formation of a double ring (A), and still less for the formation of (B) or (C).

In Graebe's model, on the other hand, any one of the three pairs of tetrahedra, connected together through two of their solid angles, can be rotated about the points through which it is connected with the other two pairs, and in this way any two adjacent free solid angles can be brought closer together until the distance between them is equal to the length of an edge of the tetrahedron, and, with it, the completion of a double ring (A) offers no difficulty.

If three pairs of tetrahedra are supposed to be rotated in the manner described above, then, in the limiting case, model I would coincide with model IV, and the distance between the two meta-positions would become equal to the length of an edge of the tetrahedron, which would render the completion of the ring (B) possible. But, as already explained, formula IV cannot be reconciled with certain facts, and the formation of a double ring (B) must therefore be regarded as improbable.

Again, even in the limiting case above supposed, the distance between the two free solid angles in the para-position is too great for the third tetrahedron to fit in between them, so that the formation of the double ring (C) is likewise improbable.

It thus appears that, of all the space formulae hitherto proposed, that of Graebe, which is nothing but a representation in space of Kekulé's well known formula, is in best agreement with the facts, and that 3-phenylene-1 : 1-diphenylphthalane, to be described presently,

contains the double ring, .

EXPERIMENTAL.

The Action of Magnesium Methyl Iodide on Diethyl Phthalate.

Diethyl phthalate (1 mol.), diluted with four times its volume of absolute ether, was added gradually to magnesium methyl iodide (4 mols.). After about twenty hours, the product was decomposed by adding ice and dilute sulphuric acid, and the ethereal layer was well washed and dried. On distilling off the ether, there remained a very viscid, dark yellow oil with a faint odour, somewhat resembling that of petroleum.

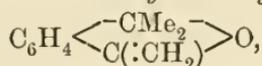
At the ordinary temperature, the oil was so viscid that it did not flow out of a vessel even when held upside down, but at about 40° it began to soften, and at about 79° became sufficiently mobile to be transferred from one vessel to another. The oil was now subjected to fractional distillation under 5 mm. pressure, when almost the whole of it distilled between 140° and 155°, and the main portion of it at 145—146°. The distillate, which had a faint yellow colour and a characteristic odour, gave the following results on analysis :

0.1911 gave 0.5805 CO₂ and 0.1249 H₂O. C = 82.85 ; H = 7.31.

0.2083 „ 0.6317 CO₂ „ 0.1443 H₂O. C = 82.71 ; H = 7.75.

C₁₁H₁₂O requires C = 82.50 ; H = 7.50 per cent.

That this substance is 1 : 1-dimethyl-3-methylenephthalan,



was proved by the study of its oxidation product. On oxidising the oil with chromic acid mixture, or by shaking with an acid solution of potassium permanganate, dimethylphthalide, C₆H₄ $\left\langle \begin{array}{c} \text{CMe}_2 \\ \text{—CO—} \end{array} \right\rangle \text{O}$, was obtained :

0.1769 gave 0.4846 CO₂ and 0.1000 H₂O. C = 74.71 ; H = 6.32.

C₁₀H₁₀O₂ requires C = 74.03 ; H = 6.23 per cent.

Dimethylphthalide has already been obtained by R. Kothe (*Annalen*, 1888, 248, 56) and H. Bauer (*Ber.*, 1904, 37, 735). The properties of my sample agreed well with the description given by these authors, except as to its melting point (69—71°), that given by Bauer being 68—69°. A similar difference in the melting point was also observed in the case of dibenzylphthalide to be described later.

The existence of a double linking in 1 : 1-dimethyl-3-methylenephthalan can be proved easily by the action of bromine on it, a solution of bromine in chloroform, when added to one of the substance in the same solvent, being decolourised at once.

The Action of Magnesium Phenyl Bromide on Diethyl Phthalate.

Precisely as in the preceding case, diethyl phthalate and magnesium phenyl bromide were mixed together in the proportion of 1 to 4 molecules, and the product was decomposed as before. After distilling off the ether, there remained a yellow, viscous oil with an odour resembling that of phenol, and showing a splendid green fluorescence. The crude oil was subjected to steam distillation in order to remove diphenyl, which was formed as a by-product. The oily residue was then fractionally distilled under 8 mm. pressure, and it was found that the first portion of the distillate, which solidified in scaly crystals, consisted of diphenyl, which had escaped distillation with

steam. The main portion distilled between 280° and 295° as a very viscous oil, and, on cooling, solidified as yellow crystals. These were recrystallised from a mixture of chloroform and ether, when small, colourless, glistening crystals melting at 194—195° were obtained:

0.2240 gave 0.7390 CO₂ and 0.1081 H₂O. C = 89.97; H = 5.39.

0.2030 „ 0.6674 CO₂ „ 0.0972 H₂O. C = 89.97; H = 5.37.

C₂₆H₁₈O requires C = 90.14; H = 5.24 per cent.

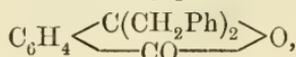
1:1-*Diphenyl-3-phenylenephthalan*, $C_6H_4 \left\langle \begin{array}{c} -CPh_2- \\ C(:C_6H_4) \end{array} \right\rangle O$, is very readily soluble in chloroform, moderately so in benzene or ether, and sparingly so in alcohol or light petroleum. Its solution decolourises neither bromine nor potassium permanganate. As already stated in the introduction, this substance doubtless contains the ring,



and a few other substances, such as carone and its derivatives, are known to contain the same ring.

The Action of Magnesium Benzyl Chloride on Diethyl Phthalate.

On decomposing the reaction product by adding ice and dilute sulphuric acid, a considerable quantity of a white, crystalline substance was obtained. It was found to be insoluble in water, alcohol, ether, or light petroleum, moderately soluble in benzene, and very soluble in chloroform, and could therefore be conveniently recrystallised from a mixture of chloroform and ether. When thus purified, it was obtained in small, colourless needles melting at 207°. Its properties agreed well with the description of dibenzylphthalide,



given by H. Bauer (*Ber.*, 1905, 38, 240), except that this author gives 204° as its melting point. An analysis of the substance left no doubt as to its being dibenzylphthalide:

0.1502 gave 0.4634 CO₂ and 0.0795 H₂O. C = 84.14; H = 5.92.

C₂₂H₁₈O₂ requires C = 84.02; H = 5.79 per cent.

On distilling off the ether from the ethereal solution separated from the aqueous layer and the crystals of dibenzylphthalide, a brown oil was left behind, which solidified to a colourless, crystalline mass. It was recrystallised from a mixture of chloroform and alcohol. Brilliant minute crystals melting at 150.5° were thus obtained:

0.1957 gave 0.6412 CO₂ and 0.1071 H₂O. C = 89.36; H = 6.12.

C₂₀H₂₄O requires C = 89.64; H = 6.23 per cent.

1:1-Dibenzyl-3-benzylidenephthalan, $C_6H_4 \left\langle \begin{array}{c} C(CH_2Ph)_2 \\ C(:CHPh) \end{array} \right\rangle O$, thus obtained, is very soluble in chloroform, moderately so in benzene or ether, and almost insoluble in alcohol or light petroleum. When oxidised with potassium permanganate, 1:1-dibenzyl-3-benzylidenephthalan is readily converted into dibenzylphthalide. The action of bromine on 1:1-dibenzyl-3-benzylidenephthalan in chloroform or carbon bisulphide solution is exactly the same as that on 1:1-dimethyl-3-methylenephthalan, and takes place very easily at the ordinary temperature.

The Action of Magnesium Ethyl Halides on Phthalic Esters.

The action of magnesium ethyl bromide and magnesium ethyl iodide on diethyl phthalate and the action of magnesium ethyl iodide on dimethyl phthalate were studied, but in these cases no phthalan derivatives were obtained, the only definite product isolated being diethylphthalide.

On the usual treatment, a brownish-yellow oil, having a disagreeable odour resembling that of onions, was obtained in each case, but on fractional distillation under 12 mm. pressure, it gave no constant boiling portion until the thermometer rose to 165°, when nearly the whole of the remaining portion distilled over. This portion, after refractionation, was analysed, with the following results, and was proved to consist of diethylphthalide:

0.2444 gave 0.6754 CO_2 and 0.1653 H_2O . $C = 75.37$; $H = 7.56$.

$C_{12}H_{14}O_2$ requires $C = 75.75$; $H = 7.43$ per cent.

Diethylphthalide, $C_6H_4 \left\langle \begin{array}{c} CEt_2 \\ -CO- \end{array} \right\rangle O$, has already been obtained by R. Kothe (*Annalen*, 1888, 248, 67) and H. Bauer (*Ber.*, 1904, 37, 735); the former isolated it as an oil boiling at 210—214°/210 mm., whilst the latter obtained it in crystals melting at 54°.

In order further to identify the above product, I prepared its mono-nitro-derivative according to the method described by Bauer. The crystals obtained melted at 104°, and agreed in this and other respects with the description given by Bauer.

Summary.

(1) In spite of the great analogy existing between phthalic acid and succinic acid, the action of the Grignard reagent on phthalic esters differs from that on succinic esters in producing derivatives of phthalide, instead of glycols.

(2) More frequently, the reaction between the Grignard reagent

and phthalic esters proceeds one step further, with the production of the derivatives of phthalan. 1:1-Dimethyl-3-methylenephthalan, 1:1-diphenyl-3-phenylenephthalan, and 1:1-dibenzyl-3-benzylidene-phthalan have thus been obtained.

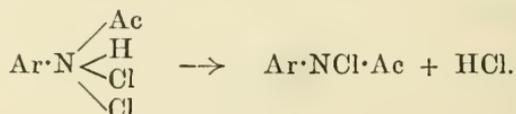
(3) Various space formulæ proposed for benzene are discussed from the point of view of the experimental results obtained in this investigation, and it is shown that Graebe's model, which represents, spatially, Kekulé's ring formula, accounts for the facts in the most satisfactory manner.

THE CHEMICAL INSTITUTE OF THE COLLEGE OF SCIENCE,
IMPERIAL UNIVERSITY OF TOKYO.

CLXIII.—*Primary Interaction* of Chlorine and Acetanilides.*

By KENNEDY JOSEPH PREVITÉ ORTON and WILLIAM JACOB JONES.

It has often been suggested that the primary union of reagents with anilines and anilides is through the nitrogen atom, subsequent changes (possibly intramolecular) leading to the formation of the substituted aniline or anilide. In the case of chlorine (or bromine), such a primary product may be a compound in which the nitrogen is quinquevalent, or the chloroamine with tervalent nitrogen formed from the first:



That the chloroamine is not, in a strict sense, an intermediary in the chlorination of anilides follows from Armstrong's discovery that the presence of hydrochloric acid is essential for the conversion of the chloroamine into the isomeric chloroacetanilide. This observation gives a strong *prima facie* case for the view that the complex in which the nitrogen is quinquevalent is the actual intermediary (compare Orton, *Proc. Roy. Soc.*, 1902, **71**, 156). It is difficult to understand, however, why hydrochloric should in that case be the only acid capable of forming with the chloroamine a salt in which the chlorine can migrate to the nucleus.*

* The more recent work of Blanksma and the views expressed by Acree will be referred to in a subsequent paper.

In the course of some experiments on the interaction of various acids (hydrochloric, hydrobromic, sulphuric, hydrofluoric, etc.) with chloroamines, it was found that chlorine could always be detected when hydrochloric acid, but not when one of the other acids, was present. This fact has led us to investigate the interaction of hydrochloric acid and chloroamines, and its converse, the primary interaction of chlorine and anilides.

It has been found that an equilibrium:



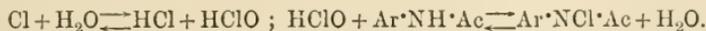
is always rapidly established in the first instance, and is then slowly disturbed by the formation of the chloroacetanilide.*

The composition of the system when in equilibrium is determined by measuring the free chlorine, by aspirating a small volume of air through the solution. Comparison of the amount of chlorine evolved in the air current with that given off by standard solutions of chlorine in the same solvent allows of a measurement of the free chlorine in the solution. The details of the method are given in the experimental part.

Our results show that the composition of the system in equilibrium depends (apart from temperature and concentration of the components) on various factors, namely, the solvent, the nature of the acyl group, and the nature and number of the constituents in the benzene nucleus. Unsubstituted acetanilide is so rapidly chlorinated that it is not possible to determine the composition of the system by this method.

Solvent.—As solvent, it is only feasible to use acetic acid, or mixtures of acetic acid and water; alcohols or acetone are attacked too rapidly by the chlorine. Although carbon tetrachloride and chloroform cannot be used for quantitative measurements, owing to the insolubility of the hydrochloric acid, it is of interest to note that when a gram-molecular proportion of this acid in aqueous

* We have not discussed in this paper the possibility that the hydrolysis of chlorine by water precedes the formation of chloroamine, or *vice versa*, that the hydrolysis of the chloroamine precedes the formation of chlorine:



Since in our numerous experiments nothing has appeared to require such intermediate reactions, we have chosen the simpler view that chlorine can directly interact with anilides, and hydrochloric acid with chloroamines. It may be mentioned that our study of chlorine solutions show that, although the small amount of hydrolysis of chlorine in aqueous solution first determined by Jakowkin (*Zeitsch. physikal. Chem.*, 1899, **29**, 626) can be readily recognised by our aspiration method, there is no indication of such a hydrolysis in solutions of acetic acid above 50 per cent. Furthermore, it is precisely in these circumstances when the hydrolysis of the chloroamine is least, namely, in glacial acetic acid, that the reaction with hydrochloric acid is most extensive.

solution is shaken with a solution of acetylchloroamino-*p*-chlorobenzene in carbon tetrachloride, *p*-chloroacetanilide, which is very slightly soluble in that medium (100 c.c. dissolve 0.03 gram at 15°), begins directly to separate.

The proportion of water has a very marked effect on the composition of the system. In glacial acetic acid (99.5 per cent.), at a concentration of 0.025 gram-molecule per litre, the right-hand side of the equation is not detectable. On adding water, reaction between the chlorine and the anilide takes place, until with 50 per cent. of water, in the case of the majority of anilides, the system consists, when the concentration is 0.025 gram-molecule per litre, nearly completely (98 per cent.) of chloroamine and hydrochloric acid (see table I):

TABLE I.

	Percentage of chlorine combined in		
	(i) 65%	(ii) 75%	(iii) 90% acetic acid.
<i>p</i> -Chloroacetanilide	—	94	—
<i>p</i> -Nitroacetanilide	63	39.5	11
2:4-Dichloroacetanilide	over 95	80	34
2:4-Dichloroformanilide	over 95	83.5	32
2:4-Dichlorobenzanilide	89	62	14
<i>s</i> -Tribromoacetanilide	over 95	86	43

The nature of the equilibrium, as well as the composition of the system, is also affected by the composition of the solvent. In 90 per cent. acetic acid a constant is given by the equation:

$$K = (c^{\text{chloroamine}} \times c^{\text{hydrochloric acid}}) / (c^{\text{chlorine}} \times c^{\text{anilide}}),$$

the concentrations being expressed in gram-molecules per litre; but with a higher proportion of water, for example, 75 per cent. acetic acid, this equation gives no constant (see table III):

TABLE II.

Values of equilibrium constants in 90 per cent. acetic acid:

	<i>K</i> .
2:4-Dichloroacetanilide	0.17
2:4-Dichloroformanilide	0.21
2:4-Dichlorobenzanilide... ..	0.028
<i>p</i> -Nitroacetanilide	0.015
<i>s</i> -Tribromoacetanilide	0.39

TABLE III.

2: 4-Dichloroacetanilide in 75 per cent. acetic acid at 15°. The equilibrium constant, $K = 6.6$, is calculated on the numbers enclosed in a rectangle :

Concentration in gram-molecules per litre.		Chlorine carried over by the air current expressed in c.c. <i>N</i> /10-solution.		"Chlorine free" expressed as a percentage of the maximum amount of chlorine obtainable from the system.	
Hydrogen chloride.	Chloroamine.	Found.	Calculated.	Found.	Calculated.
0.025	0.025	1.06	1.54	19.3	28.0
0.025	0.025	1.15	1.54	20.9	28.0
2 × 0.025	0.025	1.88	2.12	34.3	38.7
3 × 0.025	0.025	2.51	—	45.5	—
3 × 0.025	0.025	2.5	—	45.7	—
5 × 0.025	0.025	3.47	3.02	63.2	55.0

In 65 per cent. acetic acid, although a constant is not given by the above equation, the equilibrium is expressed by the equation :

$$K' = (c^{\text{chloroamine}} \times c^2 \text{hydrochloric acid}) / (c^{\text{chlorine}} \times c^{\text{anilide}}),$$

as is illustrated in table IV :

TABLE IV.

p-Nitroacetanilide in 65 per cent. acetic acid at 15°. $K' = 0.093$.

Concentration in gram-molecules per litre.		Chlorine carried over by the air current expressed in c.c. <i>N</i> /10-solution.		"Chlorine free" expressed as a percentage of the maximum amount of chlorine obtainable from the system.			
Hydrogen chloride.	Chloroamine.	Found.	Calculated on equilibrium.		Found.	Calculated on equilibrium.	
			(1) <i>K</i>	(2) <i>K'</i>		(1) <i>K</i>	(2) <i>K'</i>
0.025	0.025	2.57	3.54	2.44	32	44.2	30.4
3 × 0.025	0.025	5.44	}		68.1		
3 × 0.025	0.025	5.49					

The value of K' for 2: 4-dichloroacetanilide in 65 per cent. acetic acid is 4.47, and for 2: 4-dichlorobenzanilide, 1.06. In 75 per cent. acetic acid, the hydrochloric acid is only partly ionised,* and hence the equilibrium is not represented by either equation alone.

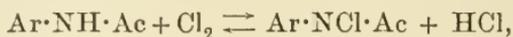
Acyl Group.—The results (table I) appear to show that the

* These facts would appear to indicate that in dilutions of acetic acid down to 90 per cent. acetic acid, hydrochloric acid, at the concentrations used, 0.006—0.1 gram-molecule per litre, is not appreciably ionised, whilst in 65 per cent. acetic acid, ionisation is complete; at intermediate concentrations of acetic acid, for example, 75 per cent., hydrochloric acid is partly ionised between the limits of the concentrations just mentioned.

acyl group has a steric effect on the equilibrium, thus the largest amount of chlorine is free when the benzoyl group is a constituent of the anilide.

Substituents in the Benzene Nucleus.—It is remarkable that the presence of two bromine atoms in the ortho-position with respect to the imino-group so greatly diminishes the proportion of free chlorine in the system (chlorine combined in 75 per cent. acetic acid = 86 per cent.). Equally remarkable is the effect of the nitro-group in the para-position (chlorine combined in 75 per cent. acetic acid = 39.5 per cent.). Measurements made with *p*-chloroacetanilide, which, owing to the rapidity of chlorination, are less exact, show that it is the nitro-group, and not the position occupied, that is singular. In the case of *p*-chloroacetanilide, the chlorine combined is greater than in the case of 2:4-dichloroacetanilide, namely, 94 instead of 80 per cent. (table I).

Effect of Acids, Chlorides, and Sodium Acetate on the Equilibrium.—Whilst the addition of sulphuric acid alone to a solution of a chloroamine does not cause the appearance of chlorine, the addition to the system:



increases slightly the proportion of uncombined chlorine. Thus, using 2:4-dichloroacetanilide, the following results are obtained in 75 per cent. acetic acid. When the concentration of the anilide and chlorine are each initially 0.025 gram-molecule, and the sulphuric acid 1.5×0.025 , the percentage of chlorine free is 23, whereas, in the absence of sulphuric acid, the percentage of chlorine free is 20.

The presence of potassium chloride (at equivalent concentrations) has very much the same effect as sulphuric acid; thus the chlorine free in 75 per cent. acetic acid is raised from 20 to 24 per cent.

The addition of sodium acetate to the system has, on the other hand, a very marked effect. Thus, in glacial acetic acid, no chlorine is combined, but in the presence of one molecular proportion of sodium acetate only 50 per cent. remains free. In 75 per cent. acetic acid, the chlorine free is similarly reduced from 20 to 10.7 per cent.

Effect of Temperature.—The effect of raising the temperature to 20° is to displace the equilibrium in favour of the anilide and chlorine. In 90 per cent. acetic acid, using dichloroacetanilide, the chlorine combined at 20° is 28 per cent., whilst at 15° it is 34 per cent. (see table V):

TABLE V.

Concentration in gram-molecules per litre.		Chlorine carried over by the air current expressed in c.c. <i>N</i> /10-solution.		"Chlorine free" expressed as a percentage of the maximum amount of chlorine obtainable from the system.	
Hydrogen chloride.	Chloroamine.	At 15°.	At 20°.	At 15°.	At 20°.
0.025	0.025	3.1	3.45	66	72
3 × 0.025	0.025	4.41	4.7	93	98
4 × 0.025	0.025	4.49	4.8	95	100

EXPERIMENTAL.

The method of measuring the free chlorine in the solution is based on the fact that a given volume of air, drawn through a solution of a gas, abstracts a quantity of gas which is proportional to the amount initially dissolved, provided that the air is saturated with the gas; or, in other words, the partial pressure of the gas in the air in contact with the solution is at a maximum. When the aspiration is at such a rate that this condition is attained, the quantity of gas abstracted is independent of the rate of aspiration.

Perman (*Trans.*, 1895, **67**, 868; 1898, **73**, 511; *Proc. Roy. Soc.*, 1903, **72**, 72) has devised methods for investigating this phenomenon, and has made a special study of solutions of ammonia.*

The apparatus which we have used in aspirating chlorine solutions was arranged as follows: Drechsel bubblers, containing the chlorine solution and the potassium iodide, together with the aspirator, which was of rather more than two litres capacity, were placed in a large constant-temperature bath. Since light accelerates greatly the attack of chlorine on acetic acid, especially when diluted, the bath was kept in a darkened room and carefully shielded. Inasmuch as the volume of air aspirated through the bubbler was determined by measuring the volume of water drawn from the aspirator, which was always filled to a given mark on the capillary tube connecting it with the second potassium iodide bubbler, no correction of the volume for the varying atmospheric pressure was necessary in our comparative experiments. The volume of "vacuum" brought in contact with the chlorine solution was constant. The air drawn through the chlorine solution was freed from dust and water vapour.

Since the extraction of chlorine would displace the equilibrium of the system, it was essential that only as small a proportion as

* Other investigations which bear on this subject have been made by Gahl (*Zeitsch. physikal. Chem.*, 1900, **33**, 178), Gans (*Zeitsch. anorg. Chem.*, 1900, **25**, 236), and McLaughlan (*Zeitsch. physikal. Chem.*, 1903, **44**, 600).

could be measured should be removed. Trials have shown that the use of 100 c.c. of solution, which completely filled the bubbler, and 250 c.c. of aspirated air permit a sufficient accuracy. Titrations of the iodine set free in similar experiments only deviate by ± 0.025 c.c. *N*/10-thiosulphate; but even then, if the solutions contain very little free chlorine, the error may amount to some units per cent.

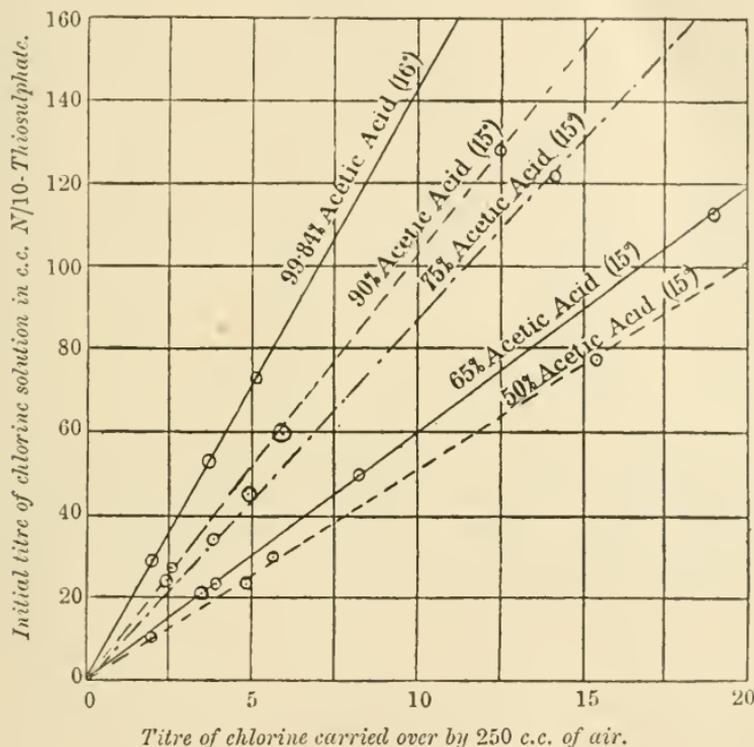
The quantity of chlorine extracted was usually less than 5 per cent. of that present in the solution, but in the most unfavourable cases as much as 10 per cent. of the free chlorine must be extracted in order to obtain a trustworthy measurement.

The 250 c.c. of air were aspirated through the solution in two and a-half minutes. The flow could be very accurately regulated and kept constant during the aspiration by a glass tap, to which a long arm used as an indicator was attached. Reduction of the time to one and a-half minutes still permitted the air to become saturated in the case of the more dilute acetic acid solutions with the form of bubbler used by us, but scarcely in glacial or 90 per cent. acetic acid.

In the experiments, the great difficulty lay in preventing change in the concentration of the standard solutions of chlorine during the manipulations. These solutions were made up in glacial acetic acid, and were transferred to a burette (100 c.c. capacity), standardised, and the appropriate volume then run into the bubbler, which contained the anilide dissolved in glacial or more dilute acetic acid, previously brought to 15°. The diluted acetic acid was made up as volumes per cent., and the change of density allowed for, so that the volume of solution in the bubbler was 100 c.c. The mixture was kept in the bath five minutes before aspiration. The procedure when chloroamine and hydrochloric acid were used was far simpler. The acid was added last to the solution of chloroamine in the bubbler; when the medium was glacial acetic acid, hydrochloric acid was necessarily in the form of a concentrated standard solution, about 20 per cent., the small volumes, in some cases less than 0.2 c.c., being measured in a standard burette graduated to 0.01 c.c. The following example shows the extent of the agreement found, on the one hand, when the system initially consists of chlorine and anilide, and, on the other, of chloroamine and hydrochloric acid; using 2:4-dichloroacetanilide in 50 per cent. acetic acid, the chlorine combined in the first case was found to be 97 per cent., and in the second 98 per cent. (see also table VI).

Aspiration of Standard Chlorine Solutions.—The standard solutions of chlorine in various dilutions of acetic acid were made up

with chlorine freed from hydrochloric acid and water, and used immediately on preparation. It was shown, however, that considerable proportions of hydrochloric acid, up to a quantity equivalent to eight times that of the chlorine, did not affect the amount of chlorine evolved in aspiration. The curves show that



the chlorine abstracted is proportional to the quantity present in the solution for concentrations of acetic acid above 50 per cent., that is, the solutions obey Henry's law. For aqueous solutions of chlorine this is not the case; an approximation to Henry's law is only found for concentrated solutions above $0.475N$; owing, doubtless, to the effect of the hydrolysis of the chlorine: $\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{Cl}^- + \text{HClO}$.

The rate of attack of chlorine on acetic acid is very slow in the dark, but becomes more rapid as water is added. It is never sufficient to interfere materially with the accuracy of our experiments. Thus the titre of 10 c.c. of a standard solution of chlorine in 75 per cent. acetic acid fell in seventy-five minutes only from 25 to 24.95 c.c. of $N/50$ -thiosulphate.

TABLE VI.

The following table shows a typical series of numbers obtained with 2:4-dichloroacetanilide in 90 per cent. acetic acid. $K=0.166$.

Concentration in gram-molecules per litre.		Chlorine carried over by the air current expressed in c.c. $N/10$ -solution.		"Chlorine free" expressed as a percentage of the maximum amount of chlorine obtainable from the system.	
Hydrogen chloride.	Chloroamine.	Found.	Calculated.	Found.	Calculated.
0.025	0.025	3.10	3.34	65.8	70.9
0.025	0.025	3.12	3.34	66.3	70.9
0.025	2×0.025	3.91	4.16	83.0	88.4
0.025	2×0.025	4.04	4.16	85.8	88.4
$\frac{1}{4} \times 0.025$	$\frac{1}{4} \times 0.025$	0.77	0.83	65.4	70.9
2×0.025	0.025	[4.16]	—	88.4	—
3×0.025	0.025	4.39	4.38	93.2	93.0
3×0.025	0.025	4.41	4.38	93.7	93.0
4×0.025	0.025	4.49	4.48	95.3	95.0
Chlorine.	Anilide.				
0.025	0.025	3.30	3.34	70.1	70.9

Our thanks are due to the British Association for a grant which has partly defrayed the cost of this investigation, and to Mr. W. C. Evans, B.Sc., who carried out most of the preliminary experiments.

UNIVERSITY COLLEGE OF NORTH WALES,
BANGOR.

CLXIV.—*The Conversion of Pinene into Sobrerol.*By GEORGE GERALD HENDERSON and WILFRED JAMES STEVENSON
EASTBURN.

As stated in a former communication, sobrerol can be obtained by oxidising pinene with aqueous mercuric acetate in the cold (Henderson and Agnew, *Trans.*, 1909, 95, 289). The pinene used for the experiments quoted in that paper showed only a small degree of optical activity, and, naturally, it was the inactive modification of sobrerol that was produced, the mixture of *d*- and *l*-pinene yielding an optically inactive mixture of *d*- and *l*-sobrerol. At the suggestion of Professor Pope, we have now examined the behaviour of *d*- and *l*-pinene towards mercuric acetate.

The *d*-pinene, obtained from Burmese oil of turpentine, was distilled in a current of steam, dried over potassium hydroxide, and fractionated with the aid of a "pear" fractionating column. The portion which distilled at 155—157° was used for oxidation; it was found to have $d_{4}^{20^{\circ}}$ 0.8599 and $[\alpha]_{D}^{20^{\circ}}$ 34.1°. The *l*-pinene was obtained from French oil of turpentine, and purified in a similar manner. The portion used for oxidation distilled at 156°; it was found to have $d_{4}^{20^{\circ}}$ 0.8606 and $[\alpha]_{D}^{20^{\circ}}$ -39.2°. Fifty grams of each specimen were oxidised with 350 grams of mercuric acetate dissolved in 1500 c.c. of water. After agitation for several days, the solutions were filtered, and the filtrates thoroughly extracted with chloroform. The chloroform extracts, after being washed with aqueous sodium carbonate and dried over anhydrous potassium carbonate, were heated until the chloroform was expelled, and there remained viscous, brown residues, which solidified on standing, and were purified by repeated crystallisations from benzene. In each case the product obtained was the inactive modification of sobrerol melting at 131°; in alcoholic solution, neither product exhibited any optical activity. Another specimen of pinene from American oil of turpentine, much more strongly dextrorotatory ($d_{4}^{20^{\circ}}$ 0.8609, $[\alpha]_{D}^{20^{\circ}}$ 13.9°) than that used in our former experiments, was also oxidised with mercuric acetate, and yielded again inactive sobrerol.

It is therefore clear that optical inversion occurs when *d*- or *l*-pinene is converted into sobrerol by the mercuric acetate method as described. However, the formation of sobrerol by this method is apparently not a case of simple oxidation of pinene. In all probability the first step in the process is the formation of an additive compound of pinene and mercuric acetate, which, under the conditions of the experiment, undergoes a subsequent change into sobrerol.

The comparative ease with which *sobrerol* can be obtained by means of mercuric acetate suggested the application of that reagent to test for the presence of pinene in Russian and in Swedish oil of turpentine. A specimen of the Russian oil was washed with aqueous sodium carbonate, distilled with steam, dried over potassium hydroxide, and fractionated with a "pear" column. A small fraction distilled at 156—157°, but the bulk of the oil had a higher boiling point. This fraction was found to have d_{4}^{20} 0.8598 and $[\alpha]_{D}^{20}$ 28.4°, and on treatment with mercuric acetate by the method described above it gave a satisfactory yield of inactive *sobrerol*; hence the specimen of Russian oil of turpentine undoubtedly contained a small proportion of *d*-pinene.

A sample of Swedish oil of turpentine was purified in a similar manner, and on distillation yielded a fairly large fraction boiling below 150° and a very small fraction boiling at 154—157°, while the bulk of the oil had a higher boiling point. The fraction which distilled at 154—157° was taken for oxidation; it was found to have d_{4}^{20} 0.7834 and $[\alpha]_{D}^{20}$ 5.7°. It did not react with mercuric acetate nearly so easily as the specimens of pinene, and only a small quantity of an oxidation product was extracted by chloroform. This product appeared to contain no *sobrerol*, and we therefore conclude that the Swedish oil of turpentine contained no pinene, or, at the most, an exceedingly small proportion.

We take this opportunity of expressing our thanks to Professor Pope for kindly supplying us with several specimens of pinene from different sources.

CHEMISTRY DEPARTMENT,
THE GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

CLXV.—*Influence of Various Sodium Salts on the Solubility of Sparingly Soluble Acids. Part II.*

By JAMES CHARLES PHILIP and FREDERICK BASIL GARNER.

IN a previous paper (Trans., 1905, 87, 987) attention was directed to the fact that the solubility of a sparingly soluble acid is markedly increased in presence of the sodium salt of a weak acid, and the experimental data then communicated showed that the magnitude of the influence of the sodium salt is closely related to the strength of the acid from which it is derived. The solubility of benzoic acid, for

instance, is greater in a sodium acetate solution than in a sodium formate solution of the same concentration, and greater in this sodium formate solution than in the corresponding sodium salicylate solution. The weaker the acid from which the sodium salt is derived, the greater is the influence of this salt on the solubility of benzoic or any other sparingly soluble acid.

The experimental work on which this general conclusion was based has been considerably extended, and the new results are communicated in the present paper. They not only confirm what has been stated in the first paragraph, but supply also further illustration of a peculiar relationship which was indicated in the course of the earlier work. It was then found that, whilst benzoic acid is considerably more soluble than salicylic acid in pure water, their positions are reversed in sodium formate solutions of greater concentration than 0.04-N. This is not an exceptional case, for several examples of the same relationship have been discovered in the course of the more recent work.

It appears, therefore, that if, of two sparingly soluble acids, the weaker is also the more soluble, then under the influence of any sodium salt the solubility of the stronger acid is increased to a greater extent than that of the other. If the difference in solubility of the two acids in water is not too great, then the curves obtained by plotting the solubility against the concentration of the sodium salt will intersect at a low value of the latter. That the occurrence of such an intersection is in harmony with the law of mass action and the theory of electrolytic dissociation was shown in the earlier paper, where a formula was deduced connecting the increase in solubility of the acid with the concentration of the added salt. Although only approximate, this formula served very well to show the general character of the influence which a sodium salt, NaA' , may be expected to exert on the solubility of an acid, HA , and to show also the relation between the solubility and the strength of the acids HA and HA' .

In the present paper the experimental values have been compared with those calculated by Noyes' equation (*Zeitsch. physikal. Chem.*, 1898, 27, 273), and it will be seen that so long as the concentration of added salt is not very great, the agreement between the two sets of values is quite good. Noyes has shown that if m_0 , m , and a_0 represent respectively the solubility of a sparingly soluble acid in pure water, the solubility in a salt solution of concentration n , and the degree of dissociation in the saturated aqueous solution, and if $x = m - m_0(1 - a_0)$, then $x^3 + rx^2 - (rn + k_a)x - k_ar = 0$. The symbol k_a represents the solubility product for the acid in question, and $r = k_a/k_a'$, k_a' being the dissociation constant of the acid from which the sodium salt is derived. As Noyes has pointed out, this formula can be deduced only by making

certain assumptions, but it may be regarded as fairly accurate so long as the acid is sparingly soluble and n is small. It is clear then that, subject to these limitations, the solubility of a sparingly soluble acid in a sodium salt solution of concentration n can be predicted, provided one knows (1) the solubility in pure water, and (2) the dissociation constants of the acid itself and of the acid from which the sodium salt is derived.

Consideration of the foregoing formulæ will show that if the experimental value of m is taken, and x is deduced by the relation $x = m - m_0(1 - a_0)$, then the equation $x^3 + rx^2 - (rn + k_a)x - k_ar = 0$ furnishes a means of finding the value of k_a . It is possible, in other words, with the help of Noyes' equation to find the dissociation constant of a weak acid by determining the influence of its sodium salt on the solubility of any sparingly soluble acid, the dissociation constant of which is known. A study of the experimental data from this point of view shows, however, that the values so obtained for the dissociation constant are subject to considerable variation; they are very sensitive to experimental error in the determination of the solubility, and can therefore be taken as indicating only the approximate magnitude of the dissociation constant.

EXPERIMENTAL.

The determinations of solubility were carried out at the temperature of $25^\circ \pm 0.1^\circ$, and the procedure adopted was that described in the earlier paper. The pure acids employed were obtained in almost all cases from Kahlbaum, and the values found for their solubility at 25° are as follows: Benzoic acid, 0.0277; salicylic acid, 0.0164; *m*-nitrobenzoic acid, 0.0205; *o*-chlorobenzoic acid, 0.0136; 3:5-dinitrobenzoic acid, 0.0062; 2:4-dinitrophenol, 0.0027. These numbers are the concentrations of the saturated aqueous solutions in gram-molecules per litre.

The results of the experimental work are summarised in the following tables, where the solubilities of the acids and the concentrations of the sodium salts are given in hundredths of a gram-molecule per litre.

TABLE I.
Sodium Acetate Solutions.

Solubility of

Concentration of sodium acetate.	Solubility of					
	Benzoic acid.	Salicylic acid.	<i>o</i> -Chloro-benzoic acid.	<i>m</i> -Nitro-benzoic acid.	3:5-Dinitro-benzoic acid.	2:4-Di-nitro-phenol.
0.00	2.77	1.64	1.36	2.05	0.62	0.27
1.19	—	—	—	—	1.60	0.97
1.23	3.76	2.61	2.30	3.08	—	—
2.96	—	—	—	—	3.17	1.62
3.06	5.13	4.29	3.95	4.75	—	—
5.91	—	—	—	—	5.67	2.37
6.13	6.95	6.92	6.68	7.55	—	—
11.85	—	—	—	—	9.98	3.51
12.28	9.77	12.17	11.67	12.44	—	—

TABLE II.

Sodium Formate Solutions.

Solubility of

Concentration of sodium formate.	Solubility of			
	Benzoic acid.	Salicylic acid.	<i>o</i> -Chloro-benzoic acid.	<i>m</i> -Nitro-benzoic acid.
0.00	2.77	1.64	1.36	2.05
1.19	3.31	2.46	—	—
1.24	—	—	2.16	2.86
2.40	3.73	3.20	—	—
3.09	—	—	3.36	3.82
5.97	4.49	5.15	—	—
6.17	—	—	4.88	5.16
11.97	5.45	7.56	—	—
12.37	—	—	7.01	7.12

TABLE III.

Sodium Monochloroacetate Solutions.

Solubility of

Concentration of sodium monochloroacetate.	Solubility of		
	Benzoic acid.	Salicylic acid.	<i>m</i> -Nitrobenzoic acid.
0.00	2.77	1.64	2.05
1.18	3.02	2.05	2.44
2.94	3.30	2.59	2.92
5.87	3.62	3.36	3.51
11.76	4.04	4.47	4.35

TABLE IV.

Sodium Succinate Solutions.

Solubility of

Concentration of sodium succinate.	Solubility of	
	Benzoic acid.	Salicylic acid.
0.00	2.77	1.64
0.73	3.35	2.15
1.81	4.19	3.14
3.61	5.38	4.75
7.21	7.38	7.84

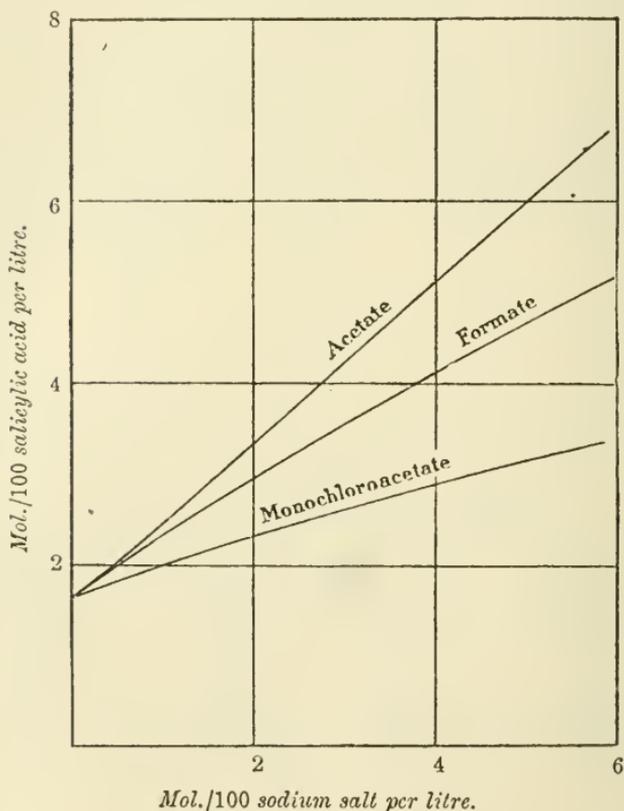
TABLE V.

Potassium Formate Solutions.

Concentration of potassium formate.	Solubility of			
	Benzoic acid.	Salicylic acid.	<i>o</i> -Chlorobenzoic acid.	<i>m</i> -Nitrobenzoic acid.
0.00	2.77	1.64	1.36	2.05
1.22	3.35	2.45	2.17	2.84
3.05	3.88	3.57	3.34	3.86
6.10	4.51	5.16	4.82	5.12

FIG. 1.

Solubility of salicylic acid in solutions of sodium acetate, formate, and monochloroacetate.



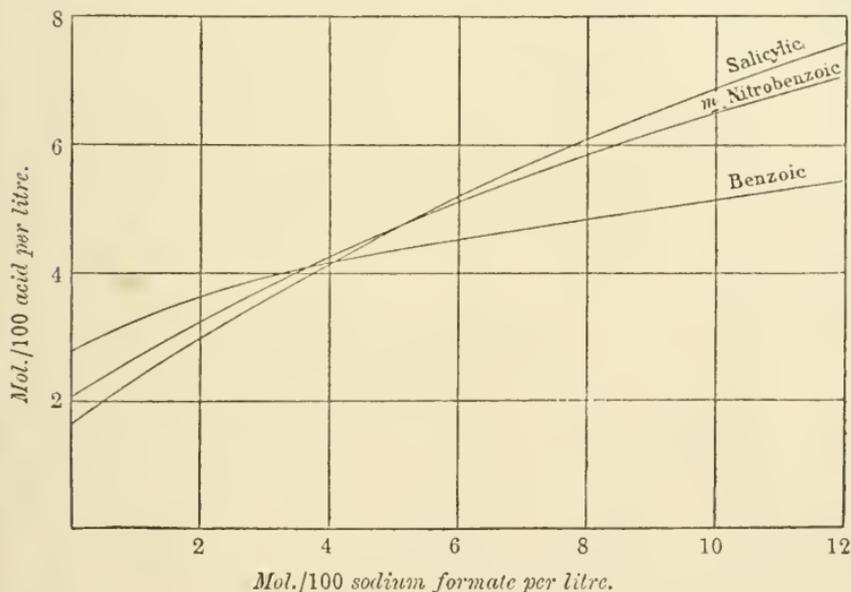
A study of the figures recorded in the tables will confirm what has already been said, namely, that the weaker the acid from which the sodium salt is derived the greater is its influence on the solubility of a sparingly soluble acid. In order to make this important point thoroughly clear, the figures relating to the influence of sodium acetate, sodium formate, and sodium monochloroacetate on the solu-

bility of salicylic acid have been plotted in Fig. 1. As is well known, monochloroacetic acid is stronger than formic acid, which in its turn is stronger than acetic acid, and the relative position of the curves in the figure is in harmony with what has been said above. Similar charts might be drawn for the acids other than salicylic acid.

An inspection of any of the tables will show that with a given added salt, it is the stronger acids which exhibit the most rapid increase in solubility. This important point is best elucidated by reference to a particular case. The figures which represent the influence of sodium formate on the solubilities of benzoic, *m*-nitrobenzoic, and salicylic acids are recorded in table II, and the corre-

FIG. 2.

Solubility of benzoic, salicylic, and m-nitrobenzoic acids in sodium formate solutions.



sponding curves are traced in Fig. 2. It should be noted that the strengths of these acids, as deduced from their dissociation constants, are very different: benzoic acid, $k=0.00006$; *m*-nitrobenzoic acid, $k=0.000345$; salicylic acid, $k=0.00102$. The weakest acid is therefore the most soluble of the three, and the strongest is the least soluble. This statement is true for pure water, but is no longer valid when the acids are dissolved in sodium formate solutions of greater concentration than $0.06-N$; under these conditions salicylic acid is the most soluble, benzoic acid the least soluble, of the three acids.

Another very striking instance of this reversal of relative solubility is furnished by the influence of sodium acetate on the solubilities of

benzoic acid ($k=0.00006$) and 3:5-dinitrobenzoic acid ($k=0.0016$). The saturated solution of benzoic acid in water at 25° is $0.0277-N$, whilst that of 3:5-dinitrobenzoic acid in water at 25° is only $0.0062-N$. In sodium acetate solutions, however, of greater concentration than $0.1-N$, dinitrobenzoic acid is more soluble than benzoic acid. Other similar cases are to be found in the material recorded in the tables.

Comparison of the figures in table V with those in table II brings out the fact that potassium and sodium formates have almost exactly the same influence on the solubilities of benzoic, salicylic, *o*-chlorobenzoic, and *m*-nitrobenzoic acids. The curve obtained by plotting the figures for the solubility of any one of these acids in potassium formate solutions practically coincides with the corresponding curve obtained from the figures for the solubility in sodium formate solutions.

The experimental values recorded in the foregoing tables furnish material, as already indicated, for testing the applicability of the formula deduced by Noyes (*loc. cit.*). The formula in question is $x^3 + rx^2 - (rn + k_a)x - k_ar = 0$, and, although not stringently exact, is much more convenient to handle than the accurate, but very complicated equation deduced by the same author. As Noyes himself has pointed out in one or two cases, the values of the solubility calculated by the simpler of the two formulæ are near enough for most purposes.

In order to make the comparison between theory and experiment, the observed figures for the solubility were first plotted, and from the curve so obtained the values of the solubility corresponding to certain salt concentrations, namely, 0.01 , 0.02 , 0.05 , and $0.1-N$, were read off. The calculated values of the solubility were obtained for each of these concentrations by the formulæ $x^3 + rx^2 - (rn + k_a)x - k_ar = 0$ and $m = x + m_0(1 - \alpha_0)$. In table VI the calculated (*A*) and experimental (*B*) values for each case are arranged side by side.

An inspection of the foregoing table shows that for solutions of salicylic, benzoic, and *o*-chlorobenzoic acids dissolved in sodium acetate and sodium formate solutions, the agreement between the calculated and the observed values is good. It is less satisfactory where *m*-nitrobenzoic acid and sodium chloroacetate solutions are involved. The deviation between the two sets of figures, apart from some cases where the difference is trifling, is such that the observed solubility is greater than the calculated solubility. This is what was found by Noyes and Chapin in the few cases in which they tested the applicability of the formula.

In a few instances the values of the solubility have been calculated by Noyes' more stringent and very complicated formula (*Zeitsch. physikal. Chem.*, 1898, 27, 273). The agreement between the calcu-

to the formation of a condensation product containing three aniline residues attached to arsenic, and differing from the additive compounds of aniline and arsenious chloride prepared by Anschütz (*Annalen*, 1891, **261**, 284), inasmuch as the latter are resolved into their generators on treatment with water or alkalis.

Triaminotriphenylarsine Oxide, $O\cdot As(C_6H_4\cdot NH_2)_3$.

A solution of 150 grams of arsenious chloride in 250 grams of benzene is added to 750 grams of aniline diluted with 250 grams of the same solvent. These materials must be thoroughly dried beforehand. A crystalline precipitate of the additive compounds is immediately formed, and gradually diminishes in bulk as the mixture is boiled for fifty hours. After leaving the product for three to eight weeks out of contact with moisture, the mixture is rendered alkaline with sodium carbonate, and the excess of aniline removed by distillation in steam. The hard resinous residue (about 22—25 grams) is dissolved in benzene, and the solution allowed to evaporate, when several crops of a crystalline substance are obtained, which, after repeated crystallisation from the same solvent, melts at 189° .

The benzene mother liquors, when concentrated considerably, yield an amorphous substance, which is also very soluble in cold chloroform, being precipitated therefrom in a viscid form by means of light petroleum. It was not found possible to crystallise this product from any of the ordinary organic solvents, but, as it was basic, purification was effected by repeatedly forming the soluble hydrochloride and precipitating the base with ammonia. The substance was thus obtained as a grey, amorphous material, readily soluble in alcohol, and precipitated therefrom by ether as a viscid mass which hardens slowly in the desiccator; it softens at 60° , and decomposes indefinitely at 108° :

0.1826 gave 0.3952 CO_2 and 0.0827 H_2O . C=59.01; H=5.03.

0.2250 „ 0.4854 CO_2 „ 0.1064 H_2O . C=58.83; H=5.25.

0.1570 „ 15.7 c.c. N_2 at 18.5° and 758 mm. N=11.53.

0.1684 „ 17.0 c.c. N_2 „ 18.5° „ 758 mm. N=11.62.

As=(i) 20.57; (ii) 20.42 (see page 1481).

$C_{18}H_{18}ON_3As$ requires C=58.85; H=4.90; N=11.44;

As=20.44 per cent.

The base is hygroscopic, and becomes soft and viscid on exposure to the atmosphere.

Triaminotriphenylarsine oxide hydrochloride,

$O\cdot As(C_6H_4\cdot NH_2, HCl)_3$,

is very soluble in water, and is precipitated as a grey, amorphous

mass by passing hydrogen chloride into a benzene solution of the base:

0.1140 gave 0.1010 AgCl. Cl=21.92.

$C_{18}H_{18}ON_3As, 3HCl$ requires Cl=22.35 per cent.

The *platinichloride* is an amorphous, yellow substance, sparingly soluble in water, and insoluble in hydrochloric acid:

0.1274 gave 0.0388 Pt. Pt=30.45.

$2C_{18}H_{18}ON_3As, 3H_2PtCl_6$ requires Pt=29.85 per cent.

Tribenzoylamino triphenylarsine oxide, $O:As(C_6H_4 \cdot NH \cdot CPh)_3$, prepared by the Schotten-Baumann reaction, dissolves readily in benzene, and is precipitated by petroleum as a light brown powder, becoming viscid on exposure to air, and melting indefinitely at 130—140°:

0.2518 gave 14.0 c.c. N_2 at 19° and 760 mm. N=6.39.

$C_{39}H_{30}O_4N_3As$ requires N=6.18 per cent.

Triacetylaminotriphenylarsine oxide, $O:As(C_6H_4 \cdot NHAc)_3$, produced by adding acetic anhydride to the base suspended in water, dissolves in benzene, and is precipitated therefrom as a grey powder, darkening at 120°, and decomposing indefinitely at 140—150°:

0.1196 gave 9.3 c.c. N_2 at 20.5° and 768 mm. N=8.97.

$C_{24}H_{24}O_4N_3As$ requires N=8.51 per cent.

Triaminotriphenylarsine oxide and the crystalline base melting at 189° are also produced when the condensation is effected in boiling toluene; the yield is about the same as in benzene, but the products obtained in the less volatile solvent are darker in colour.

The hydrochloride of the crystalline base (m. p. 189°) is only sparingly soluble in water, and in this way it can be separated from triaminotriphenylarsine oxide hydrochloride. The crystalline base separates from benzene in transparent, colourless spicules:

0.1723 gave 0.4256 CO_2 and 0.0980 H_2O . C=67.37; H=5.80.*

0.1748 „ 15.4 c.c. N_2 at 27° and 770 mm. N=9.85.

As=(i) 17.22; (ii) 17.20 (see page 1481).

$C_{24}H_{22}N_3As$ requires C=67.45; H=5.15; N=9.83;

As=17.56 per cent.

These results indicate that the substance contains four phenyl residues associated with one arsenic and three nitrogen atoms. The formulæ $C_6H_5 \cdot NH \cdot C_6H_4 \cdot As(C_6H_4 \cdot NH_2)_2$ and

$C_6H_5 \cdot NH \cdot C_6H_4 \cdot As(NH \cdot C_6H_5) \cdot C_6H_4 \cdot NH_2$

correspond with these conditions, but it was not found possible to elucidate completely the constitution of this base with the amount of material obtainable. Benzoylation led to the production of a

* Duplicates: C=67.90; C=67.84; C=67.84.

H=5.68; H=5.95; H=5.98.

dibenzoyl derivative, crystallising in colourless, refractive plates melting at 221—222°.

Tricamphorylarsinic Acid, $(C_{10}H_{15}O)_3As(OH)_2$.

Sodium camphor and arsenious chloride were condensed in dry toluene in the manner indicated in a previous communication (Trans., 1908, **93**, 2144), and the product extracted repeatedly with aqueous sodium hydroxide. After precipitation with mineral acid, the acidic products were extracted with small quantities of benzene until a residue was obtained consisting of crude dicamphorylarsinic acid (*loc. cit.*); the benzene extracts also yielded small quantities of this substance. The final brown mother liquors were evaporated to dryness, the residue dissolved in dilute aqueous sodium hydroxide, and the solution boiled with animal charcoal and concentrated to the crystallising point. The crystals, which consist of sodium dicamphorylarsinate, were removed, the solution acidified, and the viscid precipitate again subjected to the treatment with benzene and sodium hydroxide to remove further quantities of dicamphorylarsinic acid. The precipitate finally obtained was a brown, uncrystallisable solid, softening at 110°, and melting indefinitely at 130°. This acid dissolved in water containing a small amount of alcohol; it was extremely soluble in benzene, alcohol, or acetic acid, separating in a viscid condition from its concentrated solutions in these solvents. A specimen obtained by repeated treatment with benzene and sodium hydroxide, when dried in the desiccator, gave the following results:

0.1580 gave 0.3716 CO_2 and 0.1176 H_2O . C = 64.12; H = 8.27.

0.3961 „ 0.0988 $Mg_2As_2O_7$. As = 12.07.

$C_{30}H_{47}O_5As$ requires C = 64.05; H = 8.36; As = 13.34 per cent.

Tricamphorylarsinic acid, when treated with aqueous sodium hydroxide, became viscid and then dissolved, forming a very soluble sodium salt. The *silver* salt was obtained as a greyish-white precipitate on adding silver nitrate to an aqueous solution of its ammonium salt:

0.1332 gave 0.0380 Ag. Ag = 28.53.

$C_{30}H_{45}O_5Ag_2As$ requires Ag = 27.83 per cent.

When heated with excess of aqueous sodium hydroxide at 130—140°, sodium tricamphorylarsinate was hydrolysed into camphor and sodium arsenate. The toluene solution, containing the non-acidic condensation products from sodium camphor and arsenious chloride, was distilled to remove the solvent. The residue yielded a large amount of camphor and small quantities of dicamphoryl, and a substance crystallising in

well-defined hexagonal and rectangular plates (m. p. 209—210°). This product, which gave a benzoyl derivative melting at 170°, had a composition approximating to that of tribornylarsine, but the yield was so small that the compound was not further examined.

The authors desire to express their thanks to the Government Grant Committee of the Royal Society for a grant which has partly defrayed the expenses of this investigation.

ROYAL COLLEGE OF SCIENCE, LONDON,
SOUTH KENSINGTON, S.W.

CLXVII.—*The Estimation of Arsenic in Organic Compounds.*

By HARRY F. V. LITTLE, EDWARD CAHEN, and GILBERT T. MORGAN.

RECENT developments in the investigation of organic derivatives of arsenic have brought into prominence the problem of estimating this element when directly combined with carbon. Of the various methods hitherto adopted for destroying the organic matter in these substances, the following may be mentioned:

(1) Combustion of the substance mixed with soda-lime by heating in a stream of air or oxygen; the residue is dissolved in hydrochloric or nitric acid, the arsenic then precipitated as sulphide, and finally converted into magnesium pyroarsenate (La Coste and Michaelis, *Annalen*, 1880, **201**, 224).

(2) Oxidation of the organic arsenic derivative by fusion with sodium peroxide, the arsenic being estimated gravimetrically as pyroarsenate (Pringsheim, *Amer. Chem. J.*, 1904, **31**, 386).

(3) Destruction of the organic matter with nitric acid containing magnesium nitrate, when a final ignition leads to the formation of magnesium arsenate (Monthulé, *Ann. Chim. anal.*, 1904, **9**, 308).

Exception has been taken to the sodium peroxide method on the ground that at the high temperature produced by the oxidation some loss of volatile arsenic compounds may result. After a long series of experiments, the authors arrive at the conclusion that with due care in mixing and heating the reagents the loss becomes almost inappreciable, even when the oxidation is violent and the substance employed somewhat volatile.

The chief difficulty arises at a later stage of the operation,

namely, in the precipitation of magnesium ammonium arsenate in the presence of the large excess of alkali salt produced from the sodium peroxide. Contrary to expectation, the results obtained were almost uniformly too high, even when measured quantities of "magnesia mixture" and the other reagents were employed. Satisfactory values were obtained by redissolving the magnesium ammonium arsenate and reprecipitating it with ammonia, but this procedure renders the analysis very long and tedious, as the two precipitations each require considerable time for their completion.

The aqueous extract of the fusion was next acidified with hydrochloric acid and distilled with a ferrous salt in a current of hydrogen chloride in accordance with Fischer's method as modified by one of us (*Trans.*, 1904, **85**, 1001). Owing, however, to the unavoidably large bulk of solution, the volatilisation of the arsenious chloride was completed only after a lengthy distillation, and accordingly this process was abandoned in favour of a volumetric method, by means of which fairly accurate results could be obtained in a comparatively short time.

In the method ultimately found to give satisfactory results, the sodium peroxide fusion was retained, but the gravimetric estimation was superseded by a volumetric process due to Gooch and Browning (*Amer. J. Sci.*, 1890, [iii], **11**, 66).

The reaction involved may be sufficiently indicated by the following equation:



these authors having shown that the change takes place quantitatively from left to right when the liberated iodine is removed by boiling. The arsenious oxide is then titrated with standard iodine in the usual way.

Procedure.

The finely powdered substance (0.2 to 0.3 gram) is mixed in a nickel crucible with 10 to 15 grams of sodium peroxide and sodium carbonate in equal proportions, a portion of these reagents being spread over the mixture to prevent loss by projection. A gentle heat is applied for about fifteen minutes, and the fusion completed by raising the temperature to dull redness for five minutes. With careful mixing and heating, the oxidation generally takes place without fuming or detonation.

The contents of the crucible are extracted with water and rinsed into a 450 c.c. conical flask. From 25 to 31 c.c. of sulphuric acid (1:1) are added cautiously, and, if necessary, the solution is boiled down to 100 c.c., when 1 gram of potassium iodide is introduced, and the liquid further concentrated to 40 c.c. A few drops of

dilute sulphurous acid are added to destroy the last traces of iodine, and the bright green solution is diluted considerably with hot water and saturated with hydrogen sulphide. The arsenious sulphide is collected, washed about three times with hot water, dissolved off the filter with 20 c.c. of *N*/2-sodium hydroxide, and the filtrate returned to the conical flask, where it is treated with 30 c.c. of hydrogen peroxide (20 vols.), the excess of this reagent being destroyed by heating on the water-bath for ten minutes. After the frothing has subsided, a few drops of phenolphthalein are added, followed by 11 c.c. of sulphuric acid (1: 1), this quantity giving 10 c.c. in excess. One gram of potassium iodide is now added to the liquid, which should have a volume of 100 c.c., and the solution concentrated to 40 c.c., when its pale yellow colour is removed by a few drops of dilute sulphurous acid. Cold water is quickly added, and the diluted solution neutralised with 2*N*-sodium hydroxide and just acidified with sulphuric acid. The requisite amount of 11 per cent. sodium phosphate (see Note 3) is added, and the arsenite solution titrated with standard iodine and starch in the usual way.

Notes on the Method.

1. A gravimetric estimation may be effected by proceeding as far as the oxidation of the sulphide with alkaline hydrogen peroxide and then precipitating as magnesium ammonium arsenate by Austin's method (*Zeitsch. anorg. Chem.*, 1900, **23**, 146).

2. The manipulation might be simplified by estimating directly, by Gooch and Browning's method, the arsenate in the filtered aqueous extract of the fusion. The filtration of nickel hydroxide and carbonate is, however, extremely tedious, and this modification of the process does not lead to greater rapidity or accuracy. The precipitate may be rendered more amenable by oxidation to nickelic hydroxide with the aid of bromine, but the results obtained in the titration are not satisfactory.

3. The titration may be carried out in the presence of sodium hydrogen carbonate, but the addition of disodium hydrogen phosphate, which has been advocated by E. Washburn, is preferable (*J. Amer. Chem. Soc.*, 1908, **30**, 31). The volume of 11 per cent. sodium phosphate added should be equal to the number of c.c. of *N*/10-iodine required in the titration.

4. The arsenic derivatives employed in working out the method were atoxyl and hexamethyltriaminotriphenylarsine, $\text{As}[\text{C}_6\text{H}_4 \cdot \text{N}(\text{CH}_3)_2]_3$, m. p. 239—240° (Michaelis and Rabinerson, *Annalen*, 1892, **270**, 140); the latter compound has the advantage over atoxyl and many of its allies in not containing water of crystallisation. The purity

of the base was shown by its combustion: C=66.22, H=6.84, theory requiring C=66.21 and H=6.89 per cent.*

A typical selection of the analytical results are shown below in tabular form.

TABLES OF RESULTS.

Strength of Iodine Solutions.

A = 0.0969-N.	B = 0.10040-N.
C = 0.1010-N.	D = 0.04032-N.

I. *Atoxyl* (Martindale, First Sample).

H₂O = 19.3 per cent. As = 25.31 per cent. (calculated).

Substance.	C.c. iodine used.	Arsenic		
		Taken.	Found.	per cent.
0.1288	9.03 Sol. A	0.0326	0.0328	25.46
0.1735	12.05 „	0.0439	0.0438	25.22
0.2763	19.09 „	0.0699	0.0693	25.08
0.2476*	17.17 „	0.0627	0.0624	25.19
0.3030*	20.92 „	0.0767	0.0760	25.07

II. *Atoxyl* (Martindale, Second Sample).

H₂O = 25.87 per cent. As = 23.28 per cent. (calculated).

Substance.	C.c. iodine used.	Arsenic		
		Taken.	Found.	per cent.
0.2722	17.50 Sol. A	0.0634	0.0635	23.34
0.2464	16.10 „	0.0574	0.0585	23.73
0.2288	14.86 „	0.0533	0.0540	23.58
0.2518	16.27 „	0.0586	0.0591	23.46
0.2482	16.16 „	0.0578	0.0587	23.63
0.2006*	12.37 Sol. B	0.0467	0.0466	23.21
0.1964*	12.27 „	0.0457	0.0462	23.52

III. *Atoxyl* (Poulenc).

H₂O = 18.91 per cent. As = 25.44 per cent. (calculated).

Substance.	C.c. iodine used.	Arsenic		
		Taken.	Found.	per cent.
0.3260	22.88 Sol. A	0.0829	0.0831	25.49
0.2608	18.25 „	0.0663	0.0663	25.42
0.2478*	17.35 „	0.0630	0.0630	25.42
0.2814*	19.60 „	0.0716	0.0712	25.30
0.2528*	17.90 „	0.0643	0.0650	25.71
0.2486*	17.43 „	0.0632	0.0633	25.46
0.2550	17.04 Sol. B	0.0649	0.0641	25.16
0.2022	13.76 „	0.0514	0.0518	25.62
0.2368	16.03 „	0.0602	0.0603	25.48

Those estimations denoted by an asterisk were carried out on the aqueous extract of the fusion (compare Note 2, p. 1479).

As the amount of water in different samples of *atoxyl* varies con-

* The authors' thanks are due to Mr. A. Tarzey for his assistance in carrying out many of the preliminary experiments and analyses.

siderably, it was estimated for each specimen, and the theoretical percentage of arsenic calculated from this result.

IV. *Hexamethyltriaminotriphenylarsine*. As = 17·23 per cent.

Substance.	C.c. iodine used.	Arsenic		per cent.
		Taken.	Found.	
0·2934	13·23 Sol. B	0·0505	0·0498	16·98
0·2070	9·29 „	0·0357	0·0350	16·89
0·2482	11·39 „	0·0428	0·0429	17·26
0·2176	9·94 „	0·0375	0·0374	17·20
0·3198	14·33 „	0·0551	0·0540	16·87
0·2628	11·65 „	0·0453	0·0439	16·69
0·1814	8·22 Sol. C	0·0312	0·0311	17·16

V. *Dicamphorylarsinic Acid*
(Martindale).

As = 18·3 per cent.

Substance.	Iodine, Sol. C.	Found.
0·2426	11·42 c.c.	17·82
0·2148	10·15 „	17·90
0·2670	12·51 „	17·74

VI. *p-Tolylarsinic Acid*
(Martindale).

As = 34·7 per cent.

Substance.	Iodine, Sol. C.	Found.
0·1449	12·88 c.c.	33·67
0·2012	18·24 „	33·83
0·1104	lost 0·0090 H ₂ O at 125°	

VII. *Sodium Tetraiodocadylate*
(Martindale).

As = 10 per cent. for
(CH₃)₂AsO·ONa, 3½ H₂O.

Substance.	Iodine, Sol. C.	Found.
0·6912	18·78 c.c.	10·28
0·6518	17·70 „	10·28
0·6864	18·70 „	10·31

VIII. *Triaminotriphenylarsine Oxide* (Morgan and Micklethwait, p. 1474).

As = 20·44 per cent.

Substance.	Iodine, Sol. C.	Found.
0·2474	13·44 c.c.	20·57
0·3372	18·18 „	20·42

IX. *Phenyltriaminotriphenylarsine*
(Morgan and Micklethwait,
p. 1475).

As = 17·56 per cent.

Substance.	Iodine, Sol. D.	Found.
0·1552	17·68 c.c.	17·22
0·2219	25·25 „	17·20

X. *Toluene-p-sulphonyl-p-amino-phenylarsinic Acid*.

As = 20·22 ; S = 8·63 per cent.

C₇H₇·SO₂·NH·C₆H₄·AsO(OH)₂.

Substance.	Iodine, Sol. D.	Found.
0·1618	21·40 c.c.	19·99
0·2320	30·25 „	19·73
0·1968	0·1236 BaSO ₄	S = 8·62

XI. *Bis-2-aminotolyl-5-arsinic Acid*
(Burroughs, Wellcome & Co.).

As = 23·44 per cent.

(NH₂·C₇H₆)₂AsO(OH).

Substance.	Iodine, Sol. C.	Found.
0·2280	13·70 c.c.	22·76
0·3228	19·41 „	22·77

XII. *Bis-p-acetylaminophenyl-arsinic Acid*
(Burroughs, Wellcome & Co.).

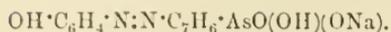
As = 19·95 per cent.

(CH₃·CO·NH·C₆H₄)₂AsO(OH).

Substance.	Iodine, Sol. C.	Found.
0·2248	11·54 c.c.	19·44
0·3558	18·40 „	19·59

XIII. *Monosodium 4-hydroxy-2'-benzeneazotoluene-5'-arsinate*
(Burroughs, Wellcome & Co.).

As = 20.95 per cent.



Substance.	Iodine, Sol. C.	Found.
0.1978	10.80 c.c.	20.67
0.2242	12.10 ,,	20.44

XIV. *Sodium 2-hydroxytolyl-5-arsinate*
(Burroughs, Wellcome & Co.).

As = 29.53 per cent.



Substance.	Iodine, Sol. D.	Found.
0.2083	40.65 c.c.	29.49
0.1405	27.00 ,,	29.05

Notes on the foregoing Estimations.

1. A substance containing little or no oxygen requires a proportionately larger amount of sodium peroxide. With hexamethyl-triaminotriphenylarsine, for example, it was found difficult to avoid a violent oxidation. This circumstance accounts for the somewhat low results usually obtained in the analysis of this base.

2. Compounds containing iodine, such as sodium tetraiodocacodylate, give rise on fusion to sodium iodate, which necessitates the addition to the acidified extract of sufficient sulphurous acid to reduce this salt to iodide, the reduction of the arsenate being then effected in the usual way.

3. *Toluene-p-sulphonyl-p-aminophenylarsinic acid* (X), which contains both arsenic and sulphur, was prepared from atoxyl by the Schotten-Baumann reaction; it dissolves very sparingly in water, although its alkali salts are extremely soluble in this solvent.

The authors desire to express their thanks to Dr. W. H. Martindale and to Dr. F. L. Pyman for their kindness in supplying specimens for analysis.

ROYAL COLLEGE OF SCIENCE, LONDON,
SOUTH KENSINGTON, S.W.

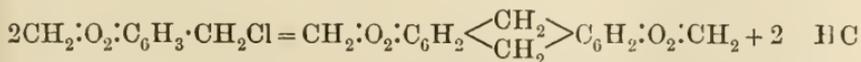
CLXVIII.—*The Action of Phosphorus Pentachloride on the Methylene Ethers of Catechol Derivatives. Part V. Derivatives of Protocatechuyl Alcohol and Protocatechuonitrile.*

By ARTHUR JAMES EWINS.

IN Part I of this series (Barger, Trans., 1908, **93**, 567) it was stated that "phosphorus pentachloride acting on piperonyl alcohol produced a tar from which nothing could be isolated." In the

course of subsequent experiments the author found, however, that if 3:4-methylenedioxybenzyl chloride, $\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_3\cdot\text{CH}_2\text{Cl}$ ("piperonyl chloride," corresponding with the alcohol), be used instead of the alcohol itself, the reaction with phosphorus pentachloride proceeds in the normal manner. 3:4-Methylenedioxybenzyl chloride has been previously obtained by Decker and Koch (*Ber.*, 1905, **38**, 1739) by passing hydrogen chloride into a cold benzene solution of piperonyl alcohol. In the present investigation it was found that this substance, on treatment with two molecular proportions of phosphorus pentachloride at 110° , is transformed to 3:4-dichloromethylenedioxybenzyl chloride, $\text{CCl}_2:\text{O}_2:\text{C}_6\text{H}_3\cdot\text{CH}_2\text{Cl}$, which by subsequent treatment with formic acid yields 3:4-carbonyldioxybenzyl chloride, $\text{CO}:\text{O}_2:\text{C}_6\text{H}_3\cdot\text{CH}_2\text{Cl}$. This cyclic carbonate has been obtained quite recently by Pauly and Alexander (*Ber.*, 1909, **42**, 2350) by the partial reduction of 3:4-carbonyldioxybenzylidene chloride ("dichloropiperonal").

The hydrolysis of 3:4-carbonyldioxybenzyl chloride to protocatechuy alcohol, $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{CH}_2\cdot\text{OH}$, was attempted. In one experiment an impure crystalline compound was obtained which had all the properties that this alcohol might be expected to possess. The substance was very readily soluble in water, alcohol, etc., but quite insoluble in benzene or xylene; its aqueous and alcoholic solutions gave an intense green coloration with ferric chloride, and the substance was easily oxidised. It was, however, found impossible to obtain the compound in a state of sufficient purity for analysis. For the preparation of 3:4-methylenedioxybenzyl chloride, the method due to Decker and Koch was employed, with a slight modification. Hydrogen chloride was passed into the dry ethereal solution of piperonyl alcohol, and the residue distilled after removal of the ether. As thus obtained, 3:4-methylenedioxybenzyl chloride was a liquid which could not readily be crystallised. In some experiments carried out in this manner there was produced on distillation a non-volatile solid, which was found to be practically insoluble in most organic solvents, and appears to be a dihydroanthracene derivative. The formation of this compound is probably due to the condensation of two molecules of 3:4-methylenedioxybenzyl chloride with elimination of hydrogen chloride, according to the equation:



It was further found that this condensation could be brought about either by the action of phosphorus pentachloride directly on piperonyl alcohol under certain conditions, or by the action of phosphoryl chloride on 3:4-methylenedioxybenzyl chloride. The

impossibility of obtaining 3:4-carbonyldioxybenzyl chloride by the direct action of phosphorus pentachloride on piperonyl alcohol is thus explained, since the phosphoryl chloride and 3:4-methylenedioxybenzyl chloride first produced would react further and bring about the above condensation. By controlling the reaction so as to minimise charring, a certain amount of the hydroanthracene derivative was actually obtained directly from piperonyl alcohol by the action of phosphorus pentachloride.

After the reduction of 3:4-methylenedioxymandelamide, $\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_3\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{NH}_2$ (Barger and Ewins, *Trans.*, 1909, **95**, 555), to an alkamine had proved unsuccessful, the action of phosphorus pentachloride on this compound was investigated. It was hoped that by this means a compound of the constitution $\text{CO}:\text{O}_2:\text{C}_6\text{H}_3\cdot\text{CHCl}\cdot\text{CN}$ (3:4-carbonyldioxyphenylchloroacetonitrile) would be obtained. By the action of four molecular proportions of phosphorus pentachloride at 130° , a mixture of compounds was produced, the main product being 3:4-methylenedioxyphenyl-dichloroacetonitrile, $\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_3\cdot\text{CCl}_2\cdot\text{CN}$, which on boiling with formic acid was converted into 3:4-methylenedioxyphenylglyoxylonitrile, $\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_3\cdot\text{CO}\cdot\text{CN}$. This compound on boiling with water readily yielded piperonylic acid. The methylene grouping in the amide was thus seen to be for the most part unattacked under the conditions employed. With more than four molecular proportions of phosphorus pentachloride, a mixture of substances was produced from which nothing could be distilled. In a recent paper by Titherley and Worrall (*Trans.*, 1909, **95**, 1143), it has been shown that phosphorus pentachloride acting on primary amides produces a mixture of compounds containing phosphorus, and the failure to obtain the desired compound from 3:4-methylenedioxymandelamide may be attributed to this fact.

The fact that 3:4-methylenedioxyphenylglyoxylonitrile was produced in the manner described above gave reason for the belief that by acting on piperonylonitrile, $\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_3\cdot\text{CN}$, with phosphorus pentachloride at a high temperature, the hitherto undescribed nitrile of protocatechuic acid might be obtained. This was indeed found to be the case. Piperonylonitrile, when acted on by two molecular proportions of phosphorus pentachloride in boiling toluene, gave, in the first place, 3:4-dichloromethylenedioxybenzonitrile, $\text{CCl}_2:\text{O}_2:\text{C}_6\text{H}_3\cdot\text{CN}$. This substance reacted in the cold with formic acid, giving 3:4-carbonyldioxybenzonitrile, $\text{CO}:\text{O}_2:\text{C}_6\text{H}_3\cdot\text{CN}$, which on boiling with water was converted into protocatechuonitrile, $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{CN}$.

EXPERIMENTAL.

3:4-Dichloromethylenedioxybenzyl Chloride, $\text{CCl}_2 \cdot \text{O}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CH}_2\text{Cl}$.

3:4-Methylenedioxybenzyl chloride (20 grams), purified by distillation under diminished pressure (b. p. $134\text{--}135^\circ/14$ mm.), was heated with two molecular proportions (49 grams) of phosphorus pentachloride to 110° for four hours. On distillation, 20 grams of a liquid (b. p. $154\text{--}156^\circ/16$ mm.) were obtained:

0.1098 gave 0.1932 AgCl. $\text{Cl} = 43.5$.

$\text{C}_8\text{H}_5\text{O}_2\text{Cl}_3$ requires $\text{Cl} = 44.4$ per cent.

As is usual in the very unstable derivatives of this type, the chlorine content is rather low.

3:4-Carbonyldioxybenzyl Chloride, $\text{CO} \cdot \text{O}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CH}_2\text{Cl}$.

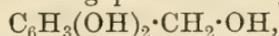
The distillate obtained as described above reacted vigorously with formic acid in the cold, and if the solution were kept moderately concentrated a crystalline solid separated almost at once. The substance was recrystallised from light petroleum (b. p. $80\text{--}90^\circ$), from which it separated in long needles, melting at 57° . Yield, 80 per cent. of the theoretical:

0.1524 gave 0.1186 AgCl. $\text{Cl} = 19.1$.

$\text{C}_8\text{H}_5\text{O}_3\text{Cl}$ requires $\text{Cl} = 19.2$ per cent.

For this substance, prepared by the careful partial reduction of 3:4-carbonyldioxybenzylidene chloride, Pauly and Alexander (*loc. cit.*) give m. p. $53.5\text{--}54^\circ$.

With the view of obtaining protocatechyl alcohol,

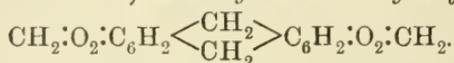


hydrolysis was carried out in the following manner.

3:4-Carbonyldioxybenzyl chloride, obtained as above, was dissolved in ten times its weight of acetone, and water added in sufficient quantity to produce a slight turbidity. Acetone was then added drop by drop until a clear solution was again produced. Slightly less than the theoretical proportion of powdered marble was added, and the mixture boiled under a reflux condenser until all the marble had become converted into calcium chloride by the hydrochloric acid produced in the reaction. The disappearance of the marble served to indicate the complete replacement of the chlorine by hydroxyl. The acetone was then removed by distillation, the aqueous residue concentrated under diminished pressure on a boiling-water bath, and the residue extracted with ether. The residue, after removal of the ether, usually consisted of a reddish-brown syrup. In one case the syrup spontaneously crystallised, but the crystals, which were coloured, could not be

freed from the mother liquor, nor could they be recrystallised, as already stated, for want of a suitable solvent; no analysis was therefore attempted. The residue left, on evaporation of the ether, was in all cases free from halogen, very soluble in water, ether, alcohol, acetone, and similar solvents, but quite insoluble in boiling benzene, toluene, xylene, or light petroleum. Its aqueous solution gave with ferric chloride a green coloration, which rapidly became brown. In alcoholic solution the green coloration was more permanent. Benzoylation, both according to Schotten-Baumann and by Einhorn's method, gave a solid product, which was evidently a mixture of benzoyl derivatives; nothing crystalline could be obtained from it. Acetylation gave similar results.

2 : 3 : 6 : 7-(or 1 : 2 : 5 : 6-)*Dimethylenetetraoxydihydroanthracene*,



As already stated, this compound may be produced in a variety of ways. Its most convenient method of preparation was found to be the following.

Piperonyl alcohol is dissolved in chloroform, and one molecular proportion of phosphorus pentachloride added to the solution. After the brisk reaction which ensues has subsided, the chloroform is removed by distillation from a boiling-water bath, and the residue heated at 100° for some time longer. A grey solid separates, which is collected and washed with a little chloroform. The solid is recrystallised from boiling nitrobenzene, in which it is sparingly soluble, and from which it separates in fine white needles, which do not melt at 360°; when heated under a pressure of 20 mm., they sublime without much decomposition. The crystals are very slightly soluble in glacial acetic acid, but almost insoluble in all other organic solvents:

0.1335 gave 0.3511 CO₂ and 0.0536 H₂O. C = 71.7; H = 4.5.

0.1353 „ 0.3523 CO₂ „ 0.0530 H₂O. C = 71.0; H = 4.5.

C₁₆H₁₂O₄ requires C = 71.6; H = 4.5 per cent.

The general properties of this substance (its sparing solubility, its volatility, and its stability), in conjunction with its formation from methylenedioxybenzyl chloride, indicate with considerable probability that it is related to anthracene; its composition, indeed, corresponds with that of a dimethylene ether of a tetrahydroxydihydroanthracene, which would be formed from two molecules of piperonyl chloride with loss of hydrogen chloride. It is, however, difficult to remove all doubt as to its constitution. A molecular weight determination was impossible, on account of its very slight solubility in organic solvents, and, partly for the same reason,

attempts to oxidise it with chromic oxide to the corresponding anthraquinone were unsuccessful. What appeared to be a well defined nitro-derivative was obtained as follows.

One gram of the substance was suspended in 8 c.c. of glacial acetic acid, and an equal volume of nitric acid (D 1.4) was added. The mixture became dark brown, oxides of nitrogen were evolved, and crystals separated out. On recrystallisation from glacial acetic acid, well-defined yellow prisms (m. p. 217°) were obtained. The substance had no acidic properties; the yield was 0.24 gram:

0.1453 gave 0.2767 CO₂ and 0.0386 H₂O. C=51.9; H=2.9.

0.2197 „ 15.6 c.c. N₂ (moist) at 20° and 760 mm.; N=8.2.

From these figures it is impossible to deduce a satisfactory formula; a *dinitro*-derivative of the original substance, of the formula C₁₆H₁₀O₄(NO₂)₂, would require C=53.6; H=2.8; N=7.8 per cent.

3:4-Methylenedioxyphenylglyoxylonitrile, CH₂:O₂:C₆H₃·CO·CN.

3:4-Methylenedioxymandelamide (5 grams) was heated with four molecular proportions of phosphorus pentachloride (22 grams) to 150—160° for four hours. On distillation, 2.5 grams of a distillate which boiled at 150°/8 mm. were obtained. With formic acid in the cold, only a very feeble reaction was observed, but on boiling a considerable evolution of hydrogen chloride was noticeable, and the solution, on cooling, deposited a crystalline solid. This was recrystallised from light petroleum (b. p. 80—90°), and then melted at 96—97°:

0.1245 gave 0.2783 CO₂ and 0.0325 H₂O. C=61.0; H=2.9.

C₈H₅O₃N requires C=61.7; H=2.85 per cent.

This compound on boiling with water yielded piperonylic acid.

3:4-Dichloromethylenedioxybenzonnitrile, CCl₂:O₂:C₆H₃·CN.

17.9 Grams of piperonylonitrile, CH₂:O₂:C₆H₃·CN, prepared by heating piperonaloxime with acetic anhydride (Marcus, *Ber.*, 1891, **24**, 3657), were dissolved in 50 c.c. of toluene, and two molecular proportions (50.8 grams) of phosphorus pentachloride added to the solution. (The use of a solvent appears to be essential.) The mixture was then boiled on a sand-bath under a reflux condenser for five hours. On distillation, 20 grams of a liquid (b. p. 155—156°/15 mm.) were obtained. This liquid, on keeping for a short time, was transformed to a solid, crystalline mass, which melted at 76—77°. The crystals are very unstable, readily evolving hydrogen chloride on exposure to moist air. To this fact may be

attributed the somewhat low value obtained for chlorine on analysis:

0.1712 gave 0.2040 AgCl. Cl=29.5.

$C_8H_3O_2NCl_2$ requires Cl=32.8 per cent.

This compound is interesting as being a crystalline dichloromethylene derivative, only one other crystalline compound of this type ($\alpha\beta$ -dichloro- α -3:4-dichloromethylenedioxyphenylethane, Barger, Trans., 1908, **93**, 2084) having hitherto been obtained.

3:4-Carbonyldioxybenzonitrile, $CO:O_2:C_6H_3:CN$.

3:4-Dichloromethylenedioxybenzonitrile reacts readily in the cold with formic acid, evolving hydrogen chloride. After a short time a crystalline solid separates, which, when recrystallised from benzene, forms broad prisms melting at 112°. Yield, 70 per cent. of the theoretical:

0.2009 gave 14.8 c.c. N_2 (moist) at 16° and 754 mm. N=8.9.

$C_8H_3O_3N$ requires N=8.7 per cent.

3:4-Dihydroxybenzonitrile (*Protocatechuonitrile*), $C_6H_3(OH)_2:CN$.

3:4-Carbonyldioxybenzonitrile was suspended in water and the mixture boiled. A brisk evolution of carbon dioxide took place, and a clear solution was finally produced. On cooling, the solution deposited crystals of protocatechuonitrile in long, white, fine needles, which, when dried in the steam-oven, melted sharply at 152°. Its aqueous solution gives the characteristic catechol colour reactions with ferric chloride:

0.2228 gave 20.1 c.c. N_2 (moist) at 18° and 759 mm. N=10.4.

$C_7H_5O_2N$ requires N=10.4 per cent.

Protocatechuonitrile yields, on benzylation by Einhorn's method, a *dibenzoyl* derivative, which crystallises from absolute alcohol in very long, fine threads, and melts at 131°.

The author wishes to express his thanks to Dr. G. Barger for his ready help and advice throughout the work.

THE WELLCOME PHYSIOLOGICAL RESEARCH LABORATORIES,
HERNE HILL, LONDON, S.E.

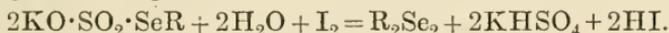
CLXIX.—*The Preparation of Disulphides. Part VI.
Note on a New Method of Preparing Disulphides.*

By THOMAS SLATER PRICE and DOUGLAS FRANK TWISS.

It is somewhat surprising that although the sodium and other salts of the alkyl thiosulphates have been known for a considerable time (Bunte, *Ber.*, 1874, **7**, 646; Purgotti, *Gazzetta*, 1890, **20**, 25; etc.), it is only comparatively recently that the reactions which they undergo have been studied to any extent. Bunte and Purgotti investigated mainly the hydrolytic action of acids with the formation of mercaptans, and Purgotti noted the complex decomposition which these compounds undergo when subjected to the action of heat.

Since 1907 the authors have been engaged in further investigations on these compounds, and have shown how the corresponding disulphides may be obtained from them (Trans., 1907, **91**, 2021; 1908, **93**, 1395, 1401, 1645; 1909, **95**, 1050). Gutmann has also studied the action of alkalis (*Ber.*, 1908, **41**, 1650), and more recently the action of acids (*Ber.*, 1909, **42**, 228).

Whilst engaged in the investigation of diselenides (*Proc.*, 1908, **24**, 134), one of us, in conjunction with Mr. L. M. Jones, B.Sc., found that these compounds are very readily produced from the alkyl selenosulphates by the action of iodine. The reaction takes place very quickly at the ordinary temperature, and proceeds according to the equation:



It has been supposed hitherto that the alkyl thiosulphates do not react with iodine; indeed, the method used by Slator (Trans., 1904, **85**, 1286; 1905, **87**, 481) and by Slator and Twiss (Trans., 1908, **93**, 1648) for determining the velocity of reaction between sodium thiosulphate and organic halogen compounds depends on the fact that the alkyl thiosulphates are not affected by iodine at the ordinary temperature. We have found, however, that at higher temperatures reaction readily takes place with the formation of the corresponding disulphides. In all probability, the reaction is direct, and does not consist in a primary hydrolysis of the alkyl thiosulphate by water and oxidation of the resulting mercaptan by iodine. It is hoped that velocity measurements will throw light on the mechanism of the reaction.

As will be seen from the experimental results, the yields of disulphide are practically quantitative. The method is much more satisfactory than the one employed by Blanksma (*Rec. trav. chim.*, 1901, **20**, 137), which depends on the interaction between sodium

disulphide and the organic halogen compound. In the case of nitro-derivatives, Blanksma has recently shown (*Rec. trav. chim.*, 1909, **28**, 105) that the nitro-group also undergoes reduction to some extent when sodium disulphide is used.

Experiments were also made in which iodine was replaced by chlorine, but the results were not very satisfactory, the disulphide obtained being contaminated to a considerable extent with the mercaptan; moreover, the yield was always poor.

The investigations detailed in our first paper (*Trans.*, 1907, **91**, 2021) have shown that the alkyl thiosulphates do not undergo electrolytic oxidation, with the formation of disulphides, at a platinum anode. We thought it possible, however, that if the solution also contained a chloride, the chlorine liberated on passage of the current would bring about the formation of disulphide. Experiments made with sodium benzyl thiosulphate and sodium *p*-nitrobenzyl thiosulphate did not, however, give very satisfactory results either in hot or cold solutions. In all cases, a small amount of a dark pasty mass was formed on the rotating platinum anode, and this was proved to contain disulphide, but at the same time, especially when an acid anolyte was used, a considerable amount of mercaptan was formed. Experiments in this direction were therefore discontinued.

EXPERIMENTAL.

Dibenzyl Disulphide.—A mixture of 5 grams of benzyl chloride, 10 grams of sodium thiosulphate, 30 c.c. of water, and 30 c.c. of alcohol (95 per cent.) was heated on the water-bath under a reflux condenser for one hour. Iodine was then added, in small portions at a time, until the colour remained, the time required for this operation being less than half an hour. The contents of the flask were then cooled to the ordinary temperature, diluted with water to precipitate any disulphide remaining in solution, and the excess of iodine removed by careful addition of sulphurous acid. The product so obtained was collected and dried; application of the usual tests showed it to be dibenzyl disulphide. The yield of crude product was 99 per cent., whereas the best yield obtained by the electrolytic method was 86 per cent.

Di-o-nitrobenzyl Disulphide.—This compound was prepared from *o*-nitrobenzyl chloride in a similar way to that already described for dibenzyl disulphide. The quantities taken were 10 grams of *o*-nitrobenzyl chloride, 15 grams of sodium thiosulphate, 40 c.c. of water, and 40 c.c. of alcohol. The reaction mixture was heated on the water-bath for one hour, and the addition of the iodine extended over half an hour.

The yield of crude di-*o*-nitrobenzyl disulphide obtained was 98·5 per cent., that is, practically quantitative. It is much better than that obtained by the action of sodium carbonate, which was only about 25 per cent. (Trans., 1908, **93**, 1401).

Experiments were not made with the meta- and para-compounds, since it was only the ortho-compound which gave very poor yields by the sodium carbonate method.

Dimethyl Dithiodiglycollate.—A mixture of 15 grams of methyl bromoacetate, 25 grams of sodium thiosulphate, 50 c.c. of water, and 50 c.c. of alcohol was heated on the water-bath for three-quarters of an hour; 50 c.c. more alcohol and 12 grams of iodine, in small portions at a time, were then added, the reaction taking place rapidly. When the reaction was complete, the mixture was cooled to the ordinary temperature, any excess of iodine removed by the addition of sulphurous acid, and then diluted with water to precipitate the dimethyl dithiodiglycollate formed. The ester was extracted with ether and recovered from the ethereal solution in the usual manner. It was proved to be dimethyl dithiodiglycollate by hydrolysis with aqueous hydrochloric acid and identification of the dithiodiglycollic acid formed.

The yield of crude ester was 73 per cent., whereas the electrolytic method gave only 60 per cent. (Trans., 1908, **93**, 1645). Moreover, there was no objectionable odour during the preparation, as was the case when the electrolytic method was used.

We desire to express our thanks to the Research Fund Committee of the Chemical Society for a grant which partly covered the cost of the foregoing investigations.

CHEMICAL DEPARTMENT,
MUNICIPAL TECHNICAL SCHOOL,
BIRMINGHAM.

CLXX.—*The Estimation of Carbonates in Presence of Nitrites, Sulphides, or Sulphites by means of Potassium Dichromate.*

By ERNEST ROBERT MARLE.

THAT carbonates are decomposed by a strong solution of potassium dichromate is probably well known, although the fact is seldom noted in the text-books, and I have found little mention of the

subject in chemical literature. Chapman Jones (*Qualitative Chemical Analysis*, 1906, 110) recommends the substitution of dichromate for dilute acid in the detection of carbonates in presence of nitrites, sulphides, or sulphites, none of which effervesce with dichromate. Moissan (*Traité de Chimie Minérale*, Vol. IV, 641) states that potassium chromate can be prepared by neutralising the dichromate with potassium carbonate.

The present research was undertaken with the view of determining if the decomposition were quantitative, to investigate the action of the dichromate on nitrites, and, if possible, to devise a method of estimating carbonates in the presence of nitrites.

EXPERIMENTAL.

I.—*The Action of Potassium Dichromate on Carbonates.*

The apparatus used consisted of a conical flask about 300 c.c. capacity, fitted with a tap funnel, and a reflux condenser, the top of which was connected with a series of drying tubes, followed by potash bulbs communicating through a calcium chloride tube with an aspirator. About 1 gram of the carbonate, in the solid state or in solution, is placed in the flask, and 5 per cent. aqueous potassium dichromate is added. The solution is heated gently to boiling, and is kept boiling for two or three minutes. Carbon dioxide is evolved fairly uniformly up to the boiling point. About 1200 c.c. of air are drawn through the apparatus at the end.

It was found that soluble carbonates are quantitatively decomposed in this way, and that insoluble carbonates, in a very fine state of division, are completely decomposed on boiling for five or ten minutes, provided that the resulting chromate is soluble in the liquid, otherwise decomposition is incomplete.

In the following table, *a* was pure sodium carbonate (from the bicarbonate); *b*, calcite; *c*, "magnesia alba ponderosa"; *d*, nickel carbonate. *c* and *d* were also analysed in the same apparatus, using sulphuric acid.

Carbonate.	Weight of carbonate in grams.	Carbon dioxide, gram.	Percentage. Calculated.
<i>a</i>	1.0895	0.4519	41.48
<i>a</i>	1.0362	0.4305	41.55
<i>a</i>	0.7894	0.3280	41.55
<i>b</i>	0.3187	0.1400	43.93
<i>b</i>	0.4365	0.1929	44.19
<i>c</i>	1.1967	0.4339	36.26
<i>c</i>	1.1389	0.4115	36.13
<i>c</i> (using acid).....	1.2787	0.4631	36.22
<i>d</i>	0.4064	0.0725	17.84
<i>d</i>	0.2877	0.0517	17.97
<i>d</i> (using acid).....	0.8506	0.1556	18.29

Copper carbonate gave 7.69, 7.47, and 7.85 per cent. of carbon dioxide, using dichromate, and 9.11 and 9.05 per cent. using acid. Barium carbonate was only partly decomposed by potassium dichromate.

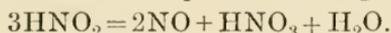
The chromates of nickel, copper, and barium are sparingly soluble or insoluble.

II.—*The Action of Potassium Dichromate on Nitrites.*

On fusion with dichromate, nitrites evolve oxides of nitrogen; the residue contains chromate, and shows no sign of reduction even when the nitrite is in excess. Strong solutions, containing a dichromate and a nitrite, evolve red fumes on boiling, and no reduction is observed unless the boiling be prolonged, when a slight brown precipitate appears (probably chromium dioxide).

Excess of a strong acid produces immediate reduction—to chromium dioxide with excess of dichromate, to a chromic salt with excess of nitrite—but as much as one-fifth equivalent of free acid* produces no reduction in half an hour. Distillation of a dilute solution of a nitrite with potassium dichromate gives an acid distillate having the reactions of nitrous acid; no nitrous fumes appear when the concentration of the nitrite is less than 5 per cent. The yield of nitrous acid increases with the concentration of the nitrite, but seems to be independent of that of the dichromate, provided that at least a quantity equivalent to the nitrite of the latter be present.

Nitrous acid is said to decompose according to the equation:



That it may be permissible to estimate carbonates in the presence of nitrites, it is necessary to determine to what extent this decomposition proceeds under the conditions of the experiment. This was done in two ways. First, the quantity of nitrous acid which can be distilled from a solution containing a nitrite and a dichromate was determined; and second, the quantity of nitric oxide evolved was measured.

The volume of standard permanganate solution required to oxidise the distillate was compared with that necessary to oxidise the original nitrite solution. It was found more satisfactory to finish the titration with oxalic acid, as, in the usual method, when excess of permanganate is present, a precipitate of hydrated peroxide of manganese is liable to be formed on warming, and this is only slowly removed by oxalic acid (compare Harcourt and Esson, *Phil. Trans.*, 1866, 156, 193).

* The nitrite contained more than 97 per cent. of sodium nitrite.

The best yield of nitrous acid was obtained when 100 c.c. of distillate were collected at a time, and the solution in the flask was made up to the original volume after each distillation.

After about 30 per cent. of the nitrous acid had passed over, successive distillates contained very slowly diminishing quantities of nitrous acid, indicating that about 90 per cent. of the total might be expected in about six litres of distillate. Mr. Chapman Jones, in 1899 (results unpublished), by distilling slowly, obtained 91.2 per cent. of the nitrous acid in the distillate, the residue in the flask containing practically no nitrite. Loss about 10 per cent.

To determine if appreciable quantities of nitric oxide are carried over during distillation, two series of experiments were made.

(1) An apparatus was employed by means of which 100 c.c. of liquid could be distilled over in an atmosphere of carbon dioxide, the gas formed being collected in a nitrometer over concentrated potassium hydroxide solution. Nitric oxide corresponding with about 3 per cent. of the nitrite was obtained.

(2) A modification of the apparatus described by Meisenheimer and Heim (*Ber.*, 1905, **38**, 3834) was used. Ten c.c. of 1.2 per cent. potassium nitrite and 25 c.c. of 1.2 per cent. potassium dichromate were placed in the flask, the air was displaced by carbon dioxide, and the liquid was distilled almost to dryness; the gas was collected in a nitrometer. A condenser was inserted between the flask and the nitrometer, as the hot nitrous acid was found to act on the mercury of the nitrometer. Nitric oxide corresponding with about 5 per cent. of the nitrite was obtained.

Since, under these rather severe conditions, the quantity of nitric oxide set free is so small, that liberated during an actual estimation of a carbonate in the presence of a nitrite would be negligible. Further, part of the nitric oxide dissolves in the dichromate solution, and gives, on boiling, the slight darkening of colour and precipitation noted above.

III.—*The Action of Potassium Dichromate on Carbonates and Nitrites together.*

From the above experiments, it would seem that it is theoretically possible to estimate carbonates in the presence of nitrites, provided that good condensation of the nitrous acid is ensured (compare Marle, *Proc.*, 1909, **25**, 74).

Equal portions of a solution of pure sodium carbonate, each containing 1.0023 grams, mixed with 25 c.c. of 5 per cent. aqueous sodium nitrite, were boiled with 100 c.c. of 5 per cent. potassium dichromate in the apparatus described on p. 1492.

The following results were obtained:

Sodium carbonate, grams.	Nitrite, grams.	Carbon dioxide, gram.	Percentage.
1·0023	1·25	0·4152	41·42
1·0023	1·25	0·4155	41·45
—	1·088	0·0170	1·56
—	2·176	0·0330	1·52
—	2·176	0·0347	1·60
0·4250	0·4419	0·1824	21·00
0·4250	0·4419	0·1837	21·14
1·0626	1·1047	0·4562	21·14
1·0626	1·1047	0·4542	21·05
2·1252	2·2093	0·9075	21·00

In the first two experiments sodium nitrite free from carbonate was used, in the remainder an impure potassium nitrite was employed. The mean of the last five determinations gives 1·30 per cent. of carbon dioxide in the nitrite. Hence a very fair accuracy is possible even when the nitrite is greatly in excess.

IV.—*The Action of Potassium Dichromate on Sulphites and Carbonates together.*

Aqueous solutions of alkali sulphites reduce potassium dichromate slowly in the cold and rapidly on boiling; no gas is evolved.

In the presence of a soluble carbonate, dichromate being in excess, an olive-green precipitate forms on standing in the cold. The filtrate contains no sulphite, and no trivalent chromium. The precipitate, thoroughly washed with cold water and dried over concentrated sulphuric acid in a vacuum, is of a brownish-green colour, insoluble in cold water. On boiling with water, carbon dioxide is evolved, and a brown powder resembling chromium dioxide remains, but a carbonate is still present.

One specimen gave on analysis: $\text{Cr}_2\text{O}_3=50\cdot34$; Alkalis= $8\cdot7$; $\text{CO}_2=15\cdot18$; $\text{H}_2\text{O}=23$ per cent., and traces of sulphate and chromate.

The substance is an impure basic carbonate of chromium, and, since chromium chromate is not soluble in potassium dichromate solution, it resembles the carbonates of nickel and barium in being incompletely decomposed by potassium dichromate solution. Experiment shows that only 98 or 99 per cent. of the carbon dioxide of a carbonate is expelled by dichromate in the presence of a sulphite, even with prolonged boiling.

The method of estimation is therefore modified by boiling the mixed solution in the apparatus, and then adding dilute sulphuric acid to complete the reaction. No sulphur dioxide is liberated.

Sodium sulphite almost always contains carbonate, so that a preliminary series of experiments was made to determine the

amount of carbonate present. Assuming this quantity, subsequent experiments gave good results for the carbon dioxide in sodium carbonate:

50.038 grams of sodium sulphite in 250 c.c.		
c.c. of solution.	Carbon dioxide, gram.	Percentage.
25	0.0605	1.21
25	0.0622	1.24
25	0.0713	1.42
50	0.1052	1.05
		Mean... 1.23

It was found impossible to use larger quantities of sulphite because of the bulky precipitate which formed in the flask.

7.5339 Grams of pure sodium carbonate and 10.0076 grams of sodium sulphite were dissolved in 250 c.c., and 25 c.c. of this solution were boiled with dichromate. The carbon dioxide due to the carbonate in the sulphite is assumed to be 0.0123 gram in each case:

Carbon dioxide, gram.	Carbon dioxide from sodium carbonate, gram.	Percentage of carbon dioxide in sodium carbonate.
0.3261	0.3138	41.65
0.3269	0.3146	41.76
0.3253	0.3130	41.55
		Na ₂ CO ₃ requires 41.51

V.—*The Action of Potassium Dichromate on Carbonates and Sulphides together.*

Sodium sulphide reduces dichromate at once, no gas is evolved, a precipitate of sulphur and chromium hydroxide forms, and the solution is yellow; when dichromate is added in excess, the filtrate decomposes carbonates.

On distillation with excess of dichromate, a neutral liquid is produced containing a white precipitate of sulphur, but no hydrogen sulphide, so that when a reflux condenser is used no gas passes on into the apparatus.

Insoluble sulphides are not affected by dichromate solution. In the presence of a soluble carbonate, a basic carbonate of chromium is formed; so that it is necessary to add dilute acid after boiling to ensure complete decomposition of the carbonate.

Pure sodium sulphide solution free from carbonate was prepared, and 5 c.c. of this (a 6 per cent. solution) were added to the pure sodium carbonate used.

Sodium carbonate, grains.	Carbon dioxide, gram.	Percentage.
0.7534	0.3139	41.66
1.3740	0.5719	41.62
		Na ₂ CO ₃ requires 41.51

Conclusions.

Carbonates may be estimated by means of potassium dichromate in the presence of nitrites. The nitrous acid formed during the operation is condensed in a reflux apparatus, and the quantity of nitric oxide (due to decomposition of the nitrous acid) carried off by the carbon dioxide is negligible under the conditions of the experiment.

If sulphides or sulphites are present, a basic carbonate of chromium is formed which is not completely decomposed by potassium dichromate, so that the action must be completed by the addition of dilute sulphuric acid towards the end of the operation.

My thanks are due to Mr. Chapman Jones for his kindness in suggesting the above problems, and for the loan of the notes of work carried out in his laboratory.

CHEMICAL DEPARTMENT,
HARTLEY UNIVERSITY COLLEGE,
SOUTHAMPTON.

CLXXI.—*The Preparation at High Temperatures of some Refractory Metals from their Chlorides.*

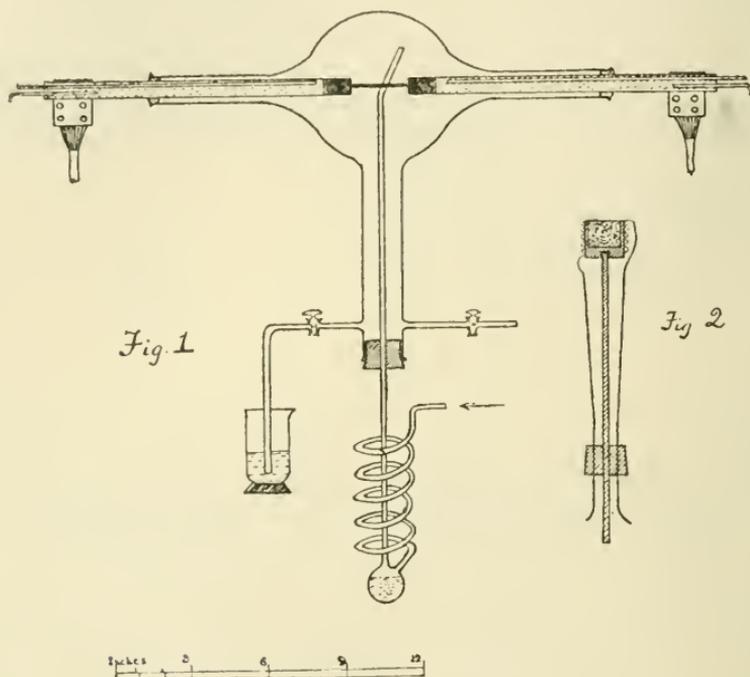
By JOHN NORMAN PRING and WILLIAM FIELDING.

VERY little has been published on the nature of the reactions whereby the metals tungsten, molybdenum, chromium, tantalum, and the non-metals, silicon and boron, may be obtained in the pure state by the dissociation of their chlorides or by decomposition of these by hydrogen at high temperatures. These reactions are made use of on a large scale in lamp manufacture for the preparation of filaments of refractory metals, and endeavours have been made to apply the method to the coating or "flashing" of carbon lamp filaments with elements which give a more favourable selective radiation than carbon.

The process devised by Just and Hanaman (*Electrical Review*, 1908, **63**, 1070; *Electrochem. and Metall. Ind.*, 1909, **7**, 24) for the preparation of tungsten filaments consists in exposing ordinary carbon filaments heated to bright redness by an electric current to an atmosphere of a volatile tungsten compound, such as a chloride or oxychloride. A uniform layer of tungsten is thereby

deposited on the filament. This is then converted into carbide by raising the temperature, and is then decomposed and all the carbon removed by heating in an atmosphere of hydrogen containing a small percentage of water vapour. In this way a sintered filament of pure tungsten is left in tubular form.

The object of this investigation was to ascertain the conditions necessary for causing the separation of tungsten, molybdenum, chromium, silicon, and boron from the chlorides, by means of a heated carbon rod, to study the extent to which they react with



the carbon at different temperatures, and to examine briefly the photometric properties of the rods coated with these deposits.

The apparatus used consisted of a tubular glass flask of about 2 litres capacity, which contained a carbon rod usually of 5 mm. diameter and about 9 cm. long (Fig. 1). To allow of electrical heating, this rod was, at each end, mounted in water-cooled brass tubes, fitted with graphite end pieces, which were fixed by electro-coppering the ends and soldering them into the brass plugs which closed the water-cooled tubes. No difficulty was in this way experienced in ensuring good electrical contact between the carbon and the graphite; arcing was quite avoided even with high-current densities, and the rod could afterwards be removed without any loss.

The water-cooled brass tubes were fixed in the side-tubes of the flask by means of wax, which proved to be quite air-tight even during the heating of the rod.

With a rod 7 cm. long and 0.5 cm. diameter in an atmosphere of hydrogen, and using a current of 160 amperes (direct current) at 18 volts, a temperature of 2200° could quite safely be attained in this apparatus, and the flask could be evacuated with the rod at 2100°. The experiments carried out with this apparatus consisted in heating the rod to various known temperatures, exposing it to the vapours of the various chlorides, either alone or in presence of hydrogen, and examining the deposits obtained.

In studying the reaction between volatile chlorides and hydrogen, the latter, before passing into the flask, was led over the surface of the chloride contained in a bulb which was kept in a water-bath to control the temperature, and hence the amount vaporised.

In cases where the chlorides were used alone, these were admitted intermittently into the vacuous flask, which was again exhausted to remove the products of decomposition. In experiments with the solid chlorides, such as tungsten and molybdenum, the substance was placed in a graphite crucible arranged 1 to 3 cm. underneath the rod, and thus vaporised by the radiant heat. In this case, pumping was continued throughout the process to maintain a diminished pressure and remove the gaseous products of decomposition. Temperature readings were taken by means of the Wanner optical pyrometer, sighted on to the carbon rod. The deviation from "black body" radiation with these heated rods was measured by checking the pyrometer readings against those given by a thermo-junction arranged in the interior of a hollow rod. The difference at 1250° was found to be not above 15° (Greenwood, *Trans.*, 1908, **93**, 1486).

In the course of an experiment, the apparatus was first completely exhausted by means of a Töpler pump, and then, while the glass was quite clear, a series of readings was taken, in each case, of the temperatures corresponding with the number of watts expended in the rod. Throughout each run the watts were kept as constant as possible in order to secure a uniform temperature.*

The first indications of the deposition of metal were usually given by a fall in the resistance of the rod, which continued as the thickness of this coating increased, and also in some cases,

* In cases where a large change in the resistance of the rod took place during the deposition, a certain error in the temperature estimates would arise through the unknown contact resistance between the carbon rod and the graphite supporting plugs. When the rod is carefully fitted, however, there is evidence to show that this contact resistance is low. An idea of the current consumption needed for

especially with tungsten and molybdenum, by a marked increase in the luminosity of the rod.

Boron.

The decomposition of boron trichloride was brought about by mixing with an excess of hydrogen and allowing to circulate through the apparatus at atmospheric pressure. At 1500° a slight deposit of free boron occurred, which fell off on cooling. At 1750° the rod began to be coated with a smooth shell deposit of boron carbide, which could afterwards be peeled off, and was identified by its characteristic hardness, enabling it to scratch a carborundum crystal. Very little change in resistance took place during this deposition.

At 1950° the deposit of carbide took place more readily, was more adherent, and assumed a nodular form, whilst at 2150° the deposit began at several centres and expanded into large, crystalline masses, which grew outwards until they met and formed an outside casing in a zone of lower temperature.

In this case, the crystals were very loosely attached to the rod, only adhering at a few small points.

At 2200° it was no longer possible to obtain a complete deposit of carbide on the rod, but a sooty formation of this substance, together with free boron, took place on the water-cooled brass holders. This dispersion of the boron carbide under these conditions is probably not due to simple volatilisation, as the melting point of this compound has been found, in the course of some unpublished work, to be as high as 2350°, and the substance does not undergo any considerable decomposition or volatilisation below 2800°.

At temperatures above 2000° the boron appears to exert a catalytic effect in converting the carbon into graphite, as, in these cases, a layer of very soft graphite was formed underneath the deposit and extended about half way through the rod, while a thin core in the centre apparently remained as unchanged carbon. The experiments made with boron trichloride are tabulated below. In each case the carbon rod used was of 5 mm. diameter, 7 to 9 cm. long, and 5 to 8 grams of boron chloride were used.

these experiments is shown in the following table, where a rod 0.49 cm. diameter and 5.5 cm. long was calibrated for temperatures up to 1760°.

Amps.	Volts.	Watts.	Temp.
50	7.7	385	1220°
60	8.7	522	1355
70	9.6	672	1470
80	10.5	840	1590
90	11.3	1017	1690
96	11.6	1113	1760

I.—*Boron trichloride used with excess of hydrogen at atmospheric pressure.*

Temp.	Length of rod, cm.	Duration of run, mins.	Thickness of layer of B_6C formed, mm.	Nature of deposit.
1800°	9	45	0.2	Smooth skin deposit.
1950	7.5	35	0.6	Nodular adherent deposit.
2200	7.0	23	—	Sooty deposit of B_6C and boron on tubes. Few crystals on rod adhering by points.
1900	8.6	25	0.5	Shell deposit studded with crystals.

II.—*Boron trichloride, with small quantity of hydrogen, at about half an atmosphere pressure.*

Temp.	Duration of run, mins.	Boron trichloride used, grams.	Nature and weight of deposit.
1780°	80	13.05	Hard adherent shell deposit with corrugated surface. Weight 0.493 gram of B_6C .
1900	50	6.21	Small, hard crystals of B_6C , weight 0.148 gram.

Silicon.

Reactions were conducted with silicon tetrachloride in a manner similar to the above. The silicon chloride was, in some cases, admitted alone after evacuation of the globe, in others was mixed with hydrogen, and in some with hydrogen and benzene vapour (compare "Helion" filament, *Electrician*, 1907, **58**, 567; *Trans. Electrochem. Soc.*, 1907, **11**, 375).

Using silicon tetrachloride alone, no considerable deposit was obtained. With an excess of hydrogen, the silicon began to deposit at 1700°, forming a thin shell layer of silicon carbide, and above this, hard crystals of free silicon, although silicon is known to combine with carbon at 1300° (Pring, *Trans.*, 1908, **93**, 2104).

At 1925° the whole of the deposit was in the form of carbide.

When the reaction was conducted in presence of benzene vapour, the deposit obtained was found to consist of silicon carbide (SiC), together with a varying excess of carbon. The method adopted, in most cases, for examining the nature of the deposits consisted in treating the substance with hot potassium hydroxide solution, whereby free silicon is dissolved. Free carbon was next removed by igniting in air, and the silicon carbide left unchanged. Analysis of this was in some cases effected by igniting in chlorine, ascertaining the loss in weight, then igniting in oxygen, and absorbing the carbon dioxide formed in a weighed potash bulb. The results of the experiments are given in the following table.

The dimensions of the rod used were, in each case, 9 cm. in length and 0.5 cm. in diameter. No considerable change in the resistance of the rod took place during the deposition.

Mixture admitted.	Length of run.	Temperature.	Nature and weight of deposit.
$\text{SiCl}_4 + \text{H}_2$	60 mins.	1700°	Shell layer of Si, studded with very small, hard crystals 0.05 mm. thick.
$\text{SiCl}_4 + \text{H}_2$	75 "	1830	Shell layers studded with very hard crystals of Si. Total weight deposited 0.248 gram.
$\text{SiCl}_4 + \text{H}_2$	60 "	1925	Large, crystalline masses of SiC deposited. Weight, 0.876 gram; graphite core, 0.485 cm. left.
$\text{SiCl}_4 + \text{H}_2$	35 "	2000	Loosely attached crystals of SiC; weight, 0.816 gram.
SiCl_4 alone	75 "	1700	No deposit.
SiHCl_3 alone	35 "	1830	No deposit. Rod evolved some gas on treating with hot potash solution.
$\text{SiHCl}_3 + \text{SiCl}_4$	40 "	2030	Considerable gas evolution on treating rod with hot potash solution.
$\text{C}_6\text{H}_6 + \text{H}_2 + \text{SiCl}_4$	40 "	1850	Very smooth shell deposit of SiC. 0.02 gram.
$\text{C}_6\text{H}_6 + \text{H}_2 + \text{SiCl}_4$	40 "	2000	Large masses of loosely adhering crystals of SiC, 0.15 cm. thick. (These, on analysis, were found to consist of SiC with excess of carbon, namely, Si=60.2 and C=36.1 per cent.)
$\text{C}_6\text{H}_6 + \text{H}_2 + \text{SiCl}_4$	60 "	2000	Crystals containing Si=63.2 per cent.
$\text{C}_6\text{H}_6 + \text{H}_2 + \text{SiCl}_4$	2 hrs.	1870	Deposit of 1.76 grams. No free Si. Combined Si in deposit = 64.4 per cent.
$\text{C}_6\text{H}_6 + \text{H}_2 + \text{SiCl}_4$	1½ "	1750	Bright crystalline deposit of 1.59 grams. Combined Si=65.5 per cent.
$\text{C}_6\text{H}_6 + \text{SiCl}_4$	1½ "	1700	Dull black, crystalline deposit, 1.35 grams.

The deposits obtained when silicon tetrachloride is decomposed in conjunction with hydrocarbons appear to consist of silicon carbide, SiC (which contains 70.3 per cent. of silicon), with an excess of carbon.

Tungsten.

Tungsten hexachloride was obtained as purple crystals contaminated with traces of the red oxychloride by passing dry chlorine over metallic tungsten, heated in a Jena glass tube. This was luted into a wider glass tube, to serve as condenser for the sublimed chloride. Great care was taken to keep everything dry and exclude moisture. The chloride, which volatilises at 346°, was placed in a graphite crucible of 3.6 cm. height, 2 cm. internal depth, 2.6 cm. internal diameter, and 3.2 cm. external diameter.

The crucible was fixed on to the end of an iron rod, as shown in Fig. 2. This and a second rod passed through two holes in the stopper at the neck of the flask, and permitted an adjustment of the distance from the heated carbon rod.

In some experiments, to facilitate further the heating of the crucible, a spiral of platinum wire was wound round, the ends being joined on to the two iron rods. A sheet of mica was placed around the crucible for insulation. The flask was then exhausted by means of a Töpler pump, and the rod heated. In some cases, hydrogen was introduced, but this was not found to assist the reaction. Probably owing to difficulties in causing volatilisation, there was usually no deposition when the pressure of gas inside the flask exceeded 2 cm.

A coating of metal on the rod began to take place at 1000° under a pressure of 1 cm. When the deposition began, an immediate fall in the resistance of the rod occurred, in many cases amounting to more than half the original value. The current was adjusted throughout each run so as to keep the watts as constant as possible. The deposits were, in all cases, of a silver-white colour, adherent and smooth, and their nature was ascertained by their hardness, the pure metal being comparatively soft and unable to mark glass, whilst the carbide is very hard and scratches glass readily (compare Moissan, "The Electric Furnace," London, 1904, p. 160).

In the experiments tabulated below, the crucible was placed at a distance of about 1 to 1.5 cm. from the rod.

Temp.	Watts consumed.	Resistance before and after (ohm.)	Duration of experiment.	Nature and weight of deposit.	
					grams.
2050°	2170	0.112 } 0.122 }	60 mins.	W ₆ C	0.35
1530	800	0.260 } 0.141 }	90 "	W	0.69
1770	1100	0.149 } 0.104 }	60 "	W ₆ C	0.18
1550	610	0.105 } 0.076 }	60 "	W ₆ C	0.86
1580	650	0.163 } 0.147 }	2½ hrs.	W	0.1
1500	580	0.260 } 0.122 }	90 mins.	W + W ₆ C	—
1400	420	0.23 } 0.10 }	60 "	W	1.13
1200	250	0.252 } 0.089 }	90 "	W	1.1

From this it is seen that metallic tungsten is deposited from the chloride at temperatures between 1000° and 1500° , and that tungsten carbide is formed above this temperature.

Molybdenum.

Reactions with molybdenum tetrachloride and pentachloride, prepared by passing dry chlorine over the heated metal, were carried out as with tungsten hexachloride. The graphite crucible was placed at a distance of 1.5 cm. from the heated rod, and the following results were obtained.

Temp.	Watts consumed.	Resistance (ohm) before and after.	Duration of experiment.	Deposit.
1600°	750	0.200 } 0.145 f	60 mins.	{ Crystalline deposit of Mo ₂ C (white).
1480	520	0.140 } 0.139 f	60 "	{ Hard, smooth deposit of Mo ₂ C (white).
1330	380	0.198 } 0.100 f	45 "	{ Metal with carbide in places, 0.3 gram.
1280	308	0.158 } 0.098 f	80 "	{ Bright smooth metallic deposit, free from car- bide.

Metallic molybdenum is thus separated from the chloride at temperatures below 1330°, the carbide being formed above this temperature.

Chromium.

An endeavour was made to obtain deposits of chromium, using the volatile oxychloride, CrO₂Cl₂. The temperature of the rod was slowly raised up to 2000°, and the pressure of oxychloride vapour varied, but no visible deposit of metal took place.

On admitting hydrogen, the mixture detonated, and chromium chloride was deposited on the sides of the flask.

The carbon rod became considerably pitted during the experiment, and on treating with aqua regia was found to have taken up traces of chromium, but no distinct coating of metal or carbide could be obtained by this reaction.

Removal of Carbon from the Carbides of Tungsten and Molybdenum.

The above experiments show that it is possible to prepare the metals tungsten and molybdenum by the dissociation of their chlorides at high temperatures. Any desired thickness of metal can, in this way, be obtained as a deposit on the carbon heaters. Endeavours were made to remove the metal deposits from the carbon rods and obtain them in the form of tubes, and, at the same time, to remove any trace of combined carbon from the metal. The authors were not successful in preparing tubes of these metals, but it was found that if the deposition of tungsten and molybdenum from the chlorides was allowed to take place on carbon rods in

presence of 1 to 2 c.c. of water vapour, the flask being otherwise vacuous, that the metal deposited at all temperatures was free from carbon, although less adherent than that prepared in absence of water vapour (compare Just and Hanaman's process, *loc. cit.*).

Photometric Measurements.

Some approximate measurements were made on the relative efficiencies of these metal-coated rods as sources of light at different temperatures.

The nature of the light radiated from heated filaments and the emissive properties of tungsten and other refractory metals have been extensively investigated by W. W. Coblentz [*Bull. of the Bureau of Standards* (Washington), 5, No. 3, p. 339].

The apparatus used in the present measurements was of the same type as that described above. The rods were mounted in the well-cleaned glass globe in which they had been prepared. An air-tight connexion between the water-cooled holders and the side-tubes of the globe was made with soft wax, and the apparatus evacuated to a pressure of 4 mm. of mercury.

A current was then passed through the rod and adjusted so that a known number of watts was expended, and the light radiated was compared photometrically with that from a standardised carbon filament lamp. A scale of "black body" temperatures corresponding with the number of watts consumed by the rod was derived optically from a carbon rod of the same size and heated under similar conditions.

In each experiment with the coated rods, readings were taken at two different temperatures, namely, 1600° and 1775°. The chief sources of inaccuracy in this work were probably the variation in the end contact resistance of the carbon, and also the fact that small, thin rods had to be employed to avoid using a current greater than 100 amperes, hence any variation in the thickness of the deposits would alter sensibly the amount of radiating surface. The carbon rods were 5.5 cm. long and 4.0 mm. in diameter, and deposits 0.25 mm. thick were generally obtained, although in the case of silicon this amounted to 0.75 mm.

During the heating, a small, steady evolution of gas took place. This effect has been observed before in experiments in which carbon rods alone were used, and is due either to occlusion of gas by the carbon, or else to the reaction of the carbon with water vapour condensed on the surface of the glass. By pumping at intervals, the pressure could be kept at 4 to 5 mm.

The photometer used was of the Lummer-Brodheim type, and the

following comparative results were obtained, the values being expressed in terms of the standardised lamp.

	Carbon rod.	Tungsten deposit.	Molybdenum deposit.	Boron deposit.
Luminous intensity with 332 watts, temp. 1600°	1.01	3.00	2.97	
Luminous intensity with 465 watts, temp. 1775°	3.40	6.06	6.27	1.16

In the case of the rod coated with silicon carbide, the value obtained was as low as 0.91. This is perhaps largely accounted for by the greater diameter of the coated rod (5.5 mm.), although the result is in great disagreement with the supposed high efficiencies of silicon-coated filaments.

With the boron and silicon deposits, the luminosity was not sufficiently high for measurement with the lower amount of power, so that results could only be obtained at the one temperature.

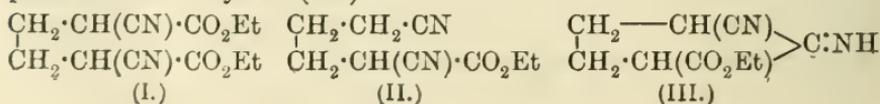
ELECTRO-CHEMICAL LABORATORY,
THE UNIVERSITY,
MANCHESTER.

CLXXII.—*The Formation and Reactions of Imino-compounds. Part X. The Formation of Imino-derivatives of Pyrrole and of isoPyrrole from Amino-nitriles.*

By STANLEY ROBERT BEST and JOCELYN FIELD THORPE.

It has been shown in Part IX of this series (Trans., 1909, 95, 685) that in an open chain of five carbon atoms having a nitrile group attached to the α - and δ -carbon atoms respectively, there is a considerable tendency to the formation of the *cyclopentane* ring. So great is this tendency, especially in the presence of sodium ethoxide or an alkaline sodium compound, that in one example investigated it was not found possible to isolate the open-chain compound, as all reactions which should have yielded it gave instead the corresponding derivative of *cyclopentane*.

Thus, ethyl $\alpha\delta$ -dicyanovalerate (I) could not be isolated from the product of the action of sodium ethoxide on ethyl $\alpha\delta$ -dicyano-adipate (II), the sole product being ethyl 2-imino-3-cyanocyclopentane-1-carboxylate (III):



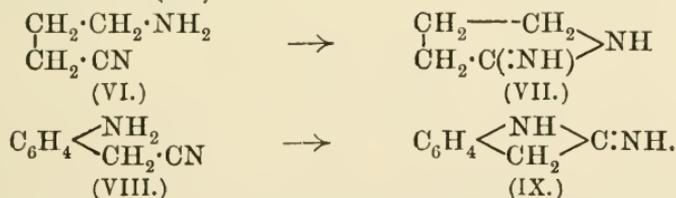
In the same manner, it was found by Moore and Thorpe (Trans., 1908, **93**, 165) that *o*-phenylenediacetonitrile (IV) passed into β -imino- α -cyanohydrindene (V) when its solution in alcohol was treated with a trace of sodium ethoxide:



This transformation is probably, therefore, general to all dinitriles of this type.

It is, of course, well known that the five-membered ring containing one nitrogen atom and four carbon atoms is also easy of formation, as is shown by the formation of lactams from γ -amino-acids, and it therefore seemed of interest to ascertain whether a cyclic compound of this type could be formed through the imino-compound in the same manner as the *cyclopentane* ring.

There are numerous examples of this kind which could be used for the purpose of ascertaining this fact. For example, γ -aminobutyronitrile (VI) might, on treatment with sodium ethoxide, pass into iminopyrrolidone (VII), and *o*-aminophenylacetonitrile (VIII) into imino-oxindole (IX).



It is proposed to investigate the conditions of ring formation from these two typical compounds in the near future, but while experiments on their formation were being instituted it was decided to investigate a similar case which was ready to hand, namely, by preparing an amino-compound of this type in the following way.

Ethyl β -imino- α -cyanoglutarate (X) has been prepared by Baron, Remfry, and Thorpe (Trans., 1904, **85**, 1737), and has been shown to react with sodium ethoxide, yielding a sodium compound represented by (XI):

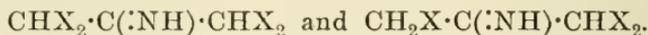


The large number of imino-compounds which we have prepared since the description of this substance was published has enabled us to gain further knowledge of its structure, and to explain the reason why the presumably more acidic hydrogen atom attached to the cyanoacetic residue contained in it is not replaced by the

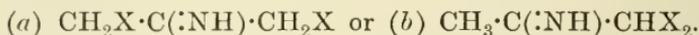
sodium atom instead of one of the hydrogen atoms of the methylene group as represented above. This explanation properly belongs to a subsequent paper which we propose publishing on the tautomerism of amino-imino-compounds, but, in order to render the present argument clear, it is necessary here to allude to certain conclusions, which may be summarised as follows.

From our experiments described in the previous parts of this series, it appears that imino-compounds may be divided into three classes.

Class I.—Comprising those compounds which have three (and presumably also four) negative groups attached to the carbon atoms adjacent to the carbimino-group, and having therefore the general formulæ:



Class II.—Comprising those compounds having two negative groups attached to the two neighbouring carbon atoms, and which therefore can have either one of the two formulæ:



Class III.—Comprising those compounds having one negative group attached to one of the carbon atoms adjacent to the carbimino-group, and which therefore have the general formula:



Now, compounds containing the imino-group react, as Collie (*Trans.*, 1897, **71**, 303) has shown in the case of ethyl β -iminobutyrate, $\text{NH}:\text{CMe} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, with dry hydrogen chloride in dry ethereal solution forming salts of the formula $:\text{C}:\text{NH}, \text{HCl}$, which, when treated with water, yield the ketone and ammonium chloride, thus:

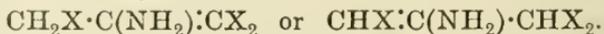


These compounds are therefore at once hydrolysed by dilute hydrochloric acid to the corresponding ketones. The members of Class III, to which, of course, ethyl β -iminobutyrate belongs, all behave in this way.

The imino-compounds of Class I, however, form isomeric salts with dry hydrogen chloride, which, when treated with water, dissociate, regenerating the imino-compound. These salts therefore have the formula $:\text{C} \cdot \text{NH}_2, \text{HCl}$, and react with water, thus:

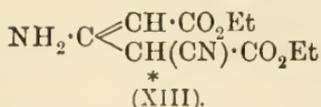
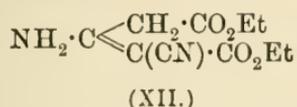


The imino-compounds of this class are therefore not hydrolysed by hydrochloric acid, and it is evident that they are amino-compounds which may have one or other of the following formulæ:



It is, moreover, evident that the first of these formulæ is the

correct one, because, taking the case of ethyl β -imino- α -cyano-glutarate, in which the two forms would be represented by formulæ (XII) and (XIII):

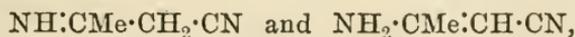


it is evident that formula (XII) represents its structure, because in a compound of formula (XIII) the hydrogen atom of the cyano-acetic residue marked (*) would most certainly be replaced by sodium on treating the compound with sodium ethoxide.

Our conclusions are then, briefly, that imino-compounds of Class III are true imino-compounds which show no chemical evidence of reacting in the amino-form, whereas compounds belonging to Class I are true amino-compounds which exhibit no chemical evidence of reacting in the imino-form.

As regards the members of Class II, the position is interesting, because they seem to react as true tautomeric amino-imino-compounds. Thus they give mixed salts of the amino- and imino-forms with dry hydrogen chloride, and their hydrolysis to the ketone by hydrochloric acid is effected after the lapse of a definite period of time. It is evident that this hydrolysis proceeds only through the imino-form of the tautomeric compound, but in the cases investigated it was always complete. The measurement therefore of the rate of hydrolysis in certain typical cases should yield valuable evidence respecting the structural conditions controlling the amino-imino-tautomerism. Preliminary experiments have shown, for example, that compounds of sub-division (a) are hydrolysed much more rapidly than those of sub-division (b).

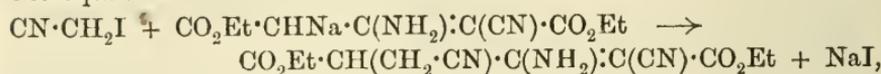
The whole question is under investigation, and will form the subject of another communication. It is, of course, probable that amino-imino-tautomerism is in reality exhibited by all these classes and is only a matter of degree, but so far as the chemical reactions of these substances are concerned we have as yet obtained no evidence in support of this view. We are, of course, aware that E. v. Meyer (*J. pr. Chem.*, 1895, [ii], 52, 83) has suggested that the two crystalline forms of β -imino- α -cyanopropane are represented by the formulæ:



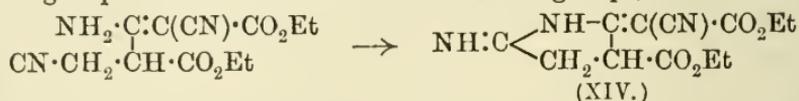
but there seems to be little evidence in support of this suggestion, because it is apparent that no reliance can be placed on the evidence afforded by the formation of the large number of derivatives of aminopyridine from this substance recently described by E. v. Meyer (*Chem. Zentr.*, 1908, ii, 591). It is well to

remember that when a compound undergoes intramolecular condensation involving, in the first instance, the production of an open-chain condensation product, no trustworthy evidence can be adduced respecting the structure of the simpler molecule. Moreover, the two forms of β -imino- α -cyanopropane react towards dry hydrogen chloride in precisely the same manner, and it is therefore probable that they are physical isomerides analogous to the two forms of ethyl β -iminobutyrate, $\text{NH}\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, which have been isolated and investigated by Behrend (*Ber.*, 1899, **32**, 544) and by Knoevenagel (*ibid.*, 853).

The sodium compound of ethyl β -imino- α -cyanoglutarate* has therefore the formula $\text{CO}_2\text{Et}\cdot\text{CHNa}\cdot\text{C}(\text{NH}_2)\cdot\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$, and when treated with iodoacetonitrile should react in accordance with the equation:

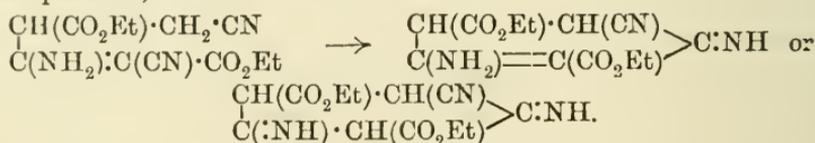


although it might be expected that the condensation product, since it had been formed in the presence of an alkaline sodium compound, would possess a ring structure due to the formation of an imino-group between the amino- and nitrile-groups, thus:



in which case the product would be ethyl 2-imino-4-carbethoxy-tetrahydropyrrolidene-5-cyanoacetate (XIV).

At the same time there is also a possibility that ring formation might take place between a nitrile group and a hydrogen atom of the methylene group, with the formation of a derivative of cyclopentane, thus:

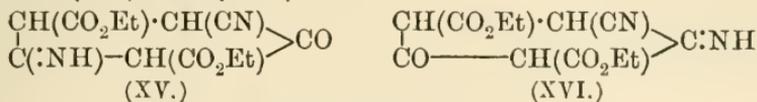


The condensation between iodoacetonitrile and the sodium compound of ethyl β -imino- α -cyanoglutarate proceeds smoothly, and a good yield of a crystalline condensation product decomposing at 205° is readily obtained. The compound possesses the expected molecular formula $\text{C}_{12}\text{H}_{15}\text{O}_4\text{N}_3$, and its physical properties show that it does not possess an open-chain structure. It reacts as an imino-compound of Class II, and is hydrolysed by hydrochloric acid to a ketone, melting at 109° , and having the molecular

* For the sake of clearness, it is proposed to retain the name of the imino-form for all these compounds irrespective of their amino- or imino-structure.

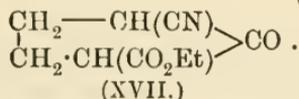
formula $C_{12}H_{14}O_5N_2$. It is evident, therefore, that the ketone has been formed from the condensation product by the hydrolysis of the group $C:NH$ to CO .

Now, if the condensation product is a derivative of *cyclopentane*, as mentioned above, this ketone must have one or other of the formulæ (XV) and (XVI):



(XV.)

(XVI.)

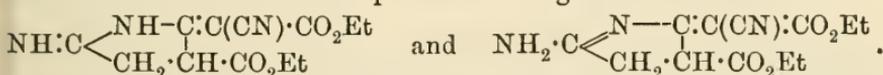


(XVII.)

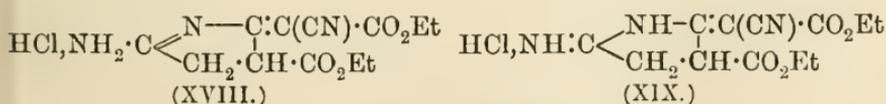
It should therefore give a violet coloration with ferric chloride, in the same way as does ethyl 5-cyanocyclopentane-1-one-2-carboxylate (XVII) (Trans., 1909, 95, 701).

The compound melting at 109° gives, however, no coloration with ferric chloride, and, moreover, the presence of another amino- or imino-group cannot be detected in it by the aid of the usual reagents. It is evident therefore that it cannot possess the *cyclopentane* structure, and it remained to ascertain whether the reactions of the condensation product conformed to those of ethyl 2-imino-4-carbethoxytetrahydropyrrolidene-5-cyanoacetate (XIV). This, as a matter of fact, they do, and there can be no question that the constitution of the condensation product decomposing at 205° is represented by this formula.

The reactions of this substance show at once that it is a tautomeric amino-imino-compound reacting in the two forms:

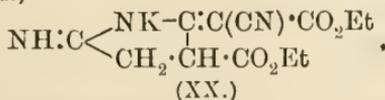


This is evident from the fact that it reacts with cold concentrated hydrochloric acid, forming a monohydrochloride (XVIII), which is, for the most part, dissociated by water, regenerating the imino-compound, although a small quantity of the ketone is formed at the same time, indicating that the imino-hydrochloride (XIX) is also formed:



(XVIII.)

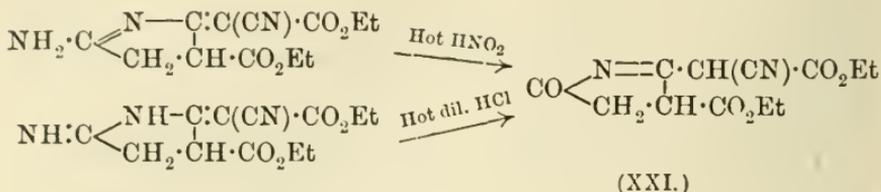
(XIX.)



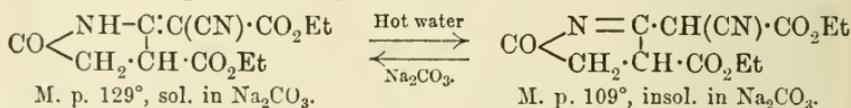
(XX.)

With boiling hydrochloric acid it is quickly hydrolysed to the ketone, the transformation being complete. It is insoluble in aqueous sodium carbonate solution, but dissolves in alkali

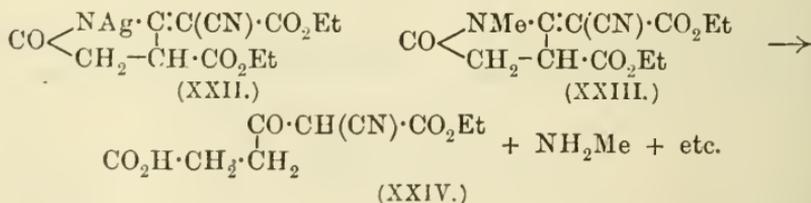
hydroxides, forming salts of the formula (XX). Nitrous acid converts it into the same ketone as is formed with hydrochloric acid:



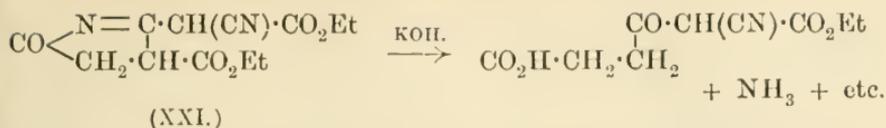
It will be noticed that the ketone is represented, not as a derivative of pyrrole, but of *isopyrrole*, namely, as ethyl 2-keto-4-carbomethoxydihydroisopyrrolyl-5-cyanoacetate (XXI). It is certain, however, that the pyrrole derivative is first formed, but at the temperature of the reaction is converted into the derivative of *isopyrrole*. This is evident from the fact that when ethyl 2-keto-4-carbomethoxydihydroisopyrrolyl-5-cyanoacetate (XXI), which is not immediately soluble in sodium carbonate solution, is dissolved by gently warming, the compound which separates on acidifying the alkaline solution melts at 129°, and differs from the compound melting at 109° in being soluble in sodium carbonate solution with effervescence. The two compounds are isomeric, and the former is converted into the latter on merely boiling with water or on heating at 100°. There is no doubt that the constitution of these substances is represented by the formulæ:



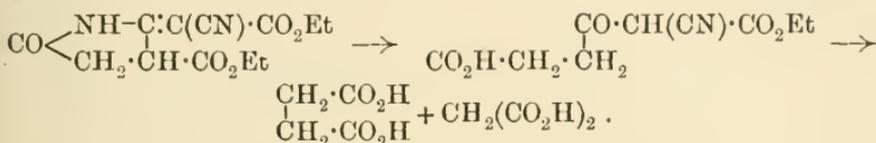
The constitution of the compound melting at 129° follows from the fact that when the silver salt (XXII) is treated with methyl iodide a methyl derivative (XXIII) is obtained, which, when hydrolysed by aqueous potassium hydroxide, yields methylamine and a compound melting at 104°, which gives a deep red coloration with ferric chloride and is evidently ethyl hydrogen α -cyano- β -keto-adipate (XXIV):



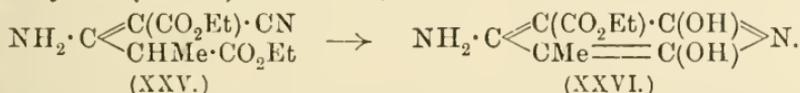
The last-named substance is the same as that which is produced by the alkaline hydrolysis of ethyl 2-keto-4-carbomethoxydihydroisopyrrolyl-5-cyanoacetate (XXI):



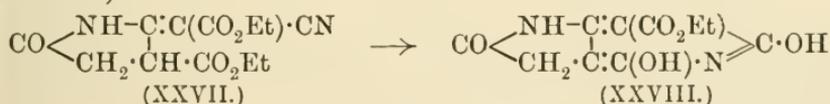
Finally, the ultimate products of the complete alkaline hydrolysis of all the compounds mentioned above are succinic and malonic acids:



With acid hydrolysing agents, ethyl 2-keto-4-carbethoxytetrahydropyrrolidene-5-cyanoacetate or its isomeride behaves in quite a different manner. It has been shown in Part I of this series (Trans., 1904, 85, 1740) that when ethyl β -imino- α -cyanoglutarate is treated with concentrated sulphuric acid, ethyl glutazincarboxylate is formed. The same reaction occurs with the monomethyl derivative (XXV), in which case ethyl methylglutazincarboxylate (XXVI) is formed, thus:

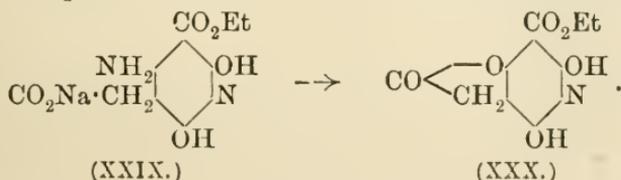


Ethyl 2-keto-4-carbethoxytetrahydropyrrolidene-5-cyanoacetate (XXVII), being a monosubstituted derivative of ethyl β -imino- α -cyanoglutarate, might therefore be expected to react in the same manner, yielding the lactam of carbethoxyglutazylacetic acid (XXVIII):



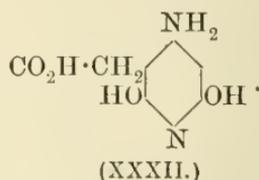
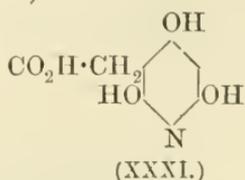
This as a matter of fact it does, the reaction taking place not only with concentrated sulphuric acid, but also on boiling for a short time with dilute sulphuric or hydrochloric acids.

The lactam of carbethoxyglutazylacetic acid (XXVIII), although insoluble in a cold solution of sodium carbonate, readily dissolves on warming, yielding a solution of the sodium salt of the amino-acid (XXIX), which, when mixed with sodium nitrite solution and poured into hot acetic acid, evolves nitrogen and



passes into the lactone of trihydroxycarbethoxypyridylacetic acid (XXX).

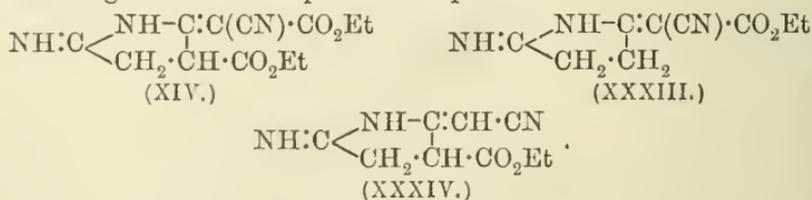
From this substance, trihydroxypyridylacetic acid (XXXI) can be readily prepared by hydrolysis with sodium hydroxide. Glutazylacetic acid (XXXII) can be prepared by the alkaline hydrolysis of the lactam of carbethoxyglutazylacetic acid (XXVIII):



Both glutazylacetic acid and trihydroxypyridylacetic acid are stable substances which do not readily pass into their anhydrides, the behaviour of these compounds being in accordance with the view previously expressed (*Trans.*, 1904, **85**, 1734), namely, that those derivatives of glutazine or of trihydroxypyridine which have both β -positions substituted react as amino- or hydroxy-compounds, whereas those which have only one β -position substituted react as tautomeric amino-imino- or keto-enolic compounds.

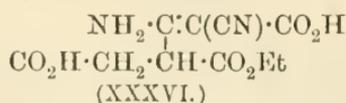
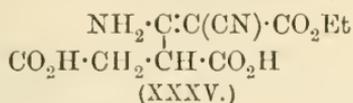
In this way, therefore, the constitution of the condensation product of iodoacetonitrile and ethyl sodio- β -imino- α -cyanoglutarate has been definitely established. Further evidence is afforded, and, moreover, more light is thrown on the nature of the isomeric oxygen derivatives mentioned above by the study of a lower series of derivatives of this substance.

This series starts with a compound, ethyl 2-iminotetrahydropyrrolidene-5-cyanoacetate (XXXIII), which can be readily prepared by the elimination of the carbethoxy-group from ethyl 2-imino-4-carbethoxytetrahydropyrrolidene-5-cyanoacetate (XIV) by a method given in the experimental portion:

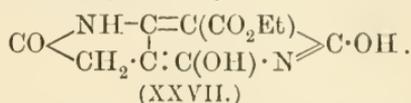
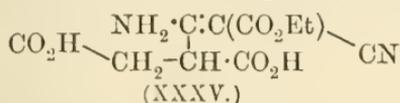


It is a crystalline basic substance, which behaves both as an amino- and as an imino-compound. It is, however, also possible that in the formation of this substance the other carbethoxyl group of the parent compound might have been affected, in which case its formula would be represented by (XXXIV). That this is not the case is shown by the fact that the corresponding dibasic acid, which is always formed to a small extent in the reaction, and

can, moreover, be readily prepared from ethyl 2-keto-4-carbethoxy-tetrahydropyrrolidene-5-cyanoacetate by careful treatment with potassium hydroxide, and must therefore have either one or other of the formulæ (XXXV) or (XXXVI):

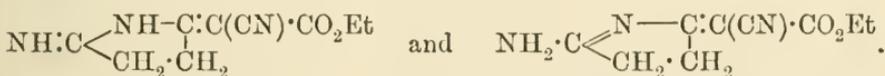


passes, when heated a few degrees above its melting point, into the lactam of carbethoxyglutazylacetic acid (XXVII):

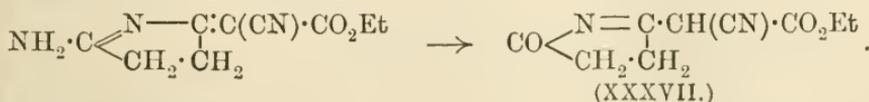


This reaction is analogous to the transformation of ethyl hydrogen β -imino- α -cyanoglutarate into ethyl glutazincarboxylate, which also takes place when the ethyl hydrogen salt is heated a few degrees above its melting point (Trans., 1904, 85, 1729). It is obvious that an acid of formula (XXXVI), in which the carboxyl and nitrile groups are attached to the same carbon atom, could not undergo this transformation.

The behaviour of ethyl 2-iminotetrahydropyrrolidene-5-cyanoacetate (XXXIII) is in every way analogous to that of the corresponding carbethoxy-derivative, and there can be no question that it is a tautomeric amino-imino-compound reacting in the two forms:

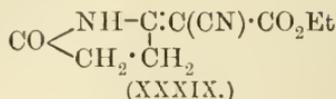
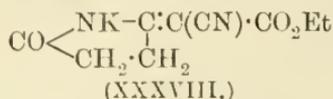


There is, however, a greater difference in the stability of the *isopyrrole* form of the oxygen derivative, which incidentally furnishes a proof that the structure of the imino-form as represented above is the correct one. Thus, when ethyl 2-iminotetrahydropyrrolidene-5-cyanoacetate (XXXII) is heated in acetic acid with nitrous acid, there is formed an oxygen derivative melting at 145°, which is insoluble in cold aqueous sodium carbonate. This is therefore the *isopyrrole* form, ethyl 2-ketodihydroisopyrrolyl-5-cyanoacetate (XXXVII):

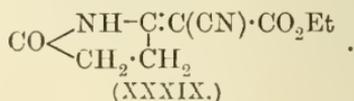
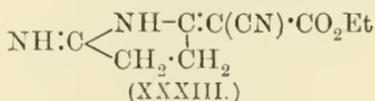


This substance, when dissolved in alcohol and treated with alcoholic potash, yields an insoluble potassium salt (XXXVIII), which, when its solution in water is acidified, gives the isomeric pyrrole derivative, ethyl 2-ketotetrahydropyrrolidene-5-cyanoacetate

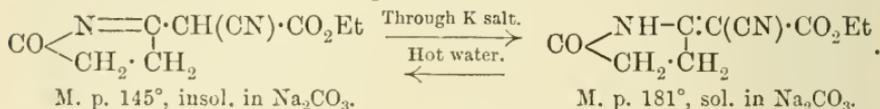
(XXXIX), which melts at 181° and dissolves in aqueous sodium carbonate with effervescence:



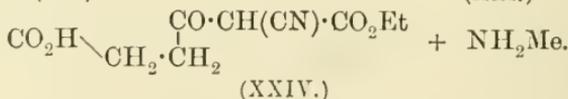
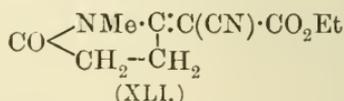
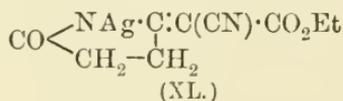
Now, when ethyl 2-iminotetrahydropyrrolidene-5-cyanoacetate (XXXIII) is hydrolysed to the oxygen derivative by hot dilute hydrochloric acid, that is, through the imino-form, the pyrrole form of the ketone, melting at 181°, is obtained:



This, therefore, is fairly definite evidence that the structure of the imino-form is that given above. The isolation of the pyrrole form in this reaction is rendered possible because this form is much more stable than is the case in the corresponding carbethoxy-derivative, as is shown by the fact that it is necessary to boil the *isopyrrole* modification for some time with water before it is completely transformed into the derivative of *isopyrrole*. The changes, as in the former case, are represented thus:



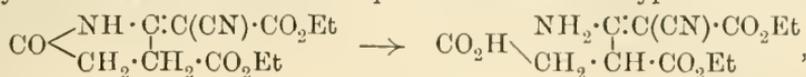
The *isopyrrole* modification, when methylated through the silver salt (XL), yields a methyl derivative (XLI), which, when boiled with aqueous potassium hydroxide, is transformed into methylamine and ethyl hydrogen α -cyano- β -keto adipate (XXIV):



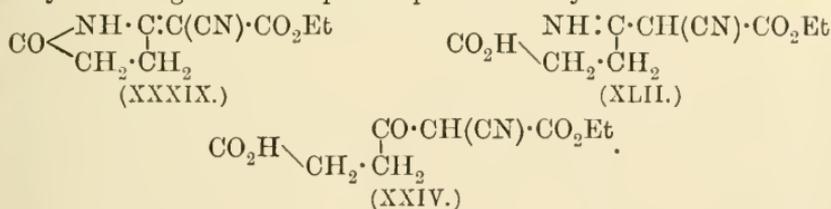
The last-named compound is identical with the acid of this formula, prepared in the manner mentioned on page 1513, only in the present instance it is possible to follow the decomposition more closely, for the following reasons:

It has already been mentioned that imino-compounds having three negative groups attached to the carbon atoms adjacent to the carbimino-group seem to react only as amino-compounds, whereas those which have only two negative groups attached to these carbon atoms react as tautomeric amino-imino-compounds. Now the open-chain compound which would be formed on breaking

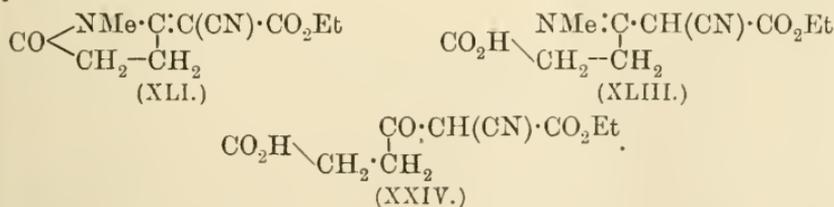
the pyrrole ring of ethyl 2-keto-4-carbethoxytetrahydropyrrolidene-5-cyanoacetate would be a compound of the first type:



and should, like γ -amino-acids, show little tendency to exist in the open-chain form. The product of ring fission from ethyl 2-keto-tetrahydropyrrolidene-5-cyanoacetate would, on the other hand, be an imino-compound of the second type, and when once the ring is broken the open-chain compound should be quite stable owing to the production of the imino-form, or, rather, of that form exhibiting amino-imino-tautomerism. This is, as a matter of fact, the case, for whereas ethyl 2-keto-4-carbethoxytetrahydropyrrolidene-5-cyanoacetate is quite stable towards sodium carbonate unless boiled for a long period of time, the ring of ethyl 2-keto-tetrahydropyrrolidene-5-cyanoacetate (XXXIX) is at once broken on merely warming with aqueous sodium carbonate, yielding ethyl hydrogen β -imino- α -cyano adipate (XLII), and from this compound ethyl hydrogen α -cyano- β -keto adipate (XXIV) can be prepared by gently warming it with aqueous potassium hydroxide:

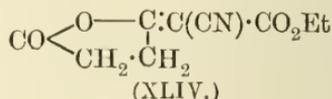
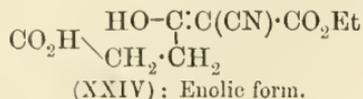


The degradation of the methyl derivative, ethyl 2-keto-1-methyl-tetrahydropyrrolidene-5-cyanoacetate (XLI), can also be followed in the same way. Thus, when warmed with aqueous sodium carbonate, it is converted into ethyl hydrogen α -cyano- β -methylimino-adipate (XLIII), from which ethyl hydrogen α -cyano- β -keto adipate (XXIV) and methylamine are produced by the action of potassium hydroxide:



A considerable temperature is necessary in order again to close the pyrrole ring in these compounds, but both the above imino- and methylimino-derivatives are reconverted into the corresponding derivatives of pyrrole on distillation under ordinary pressure. The same behaviour is exhibited by ethyl hydrogen α -cyano- β -keto-

adipate (XXIV), in which there is, of course, keto-enolic tautomerism, for, although it exists as the keto-enolic acid under ordinary conditions, yet it readily passes on distillation into the corresponding lactone (XLIV), from which the ketonic acid is regenerated by the action of alkalis:



From these experiments it is reasonable to conclude that only those open-chain compounds which have an amino-group in the γ -position with respect to a nitrile group will yield imino-derivatives of pyrrole on treatment with sodium ethoxide, and that those substances which are tautomeric amino-imino-compounds will not yield cyclic imino-derivatives under these conditions.

EXPERIMENTAL.

Ethyl β -Imino- α -cyanoglutarate,
 $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{C}(:\text{NH})\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}.$

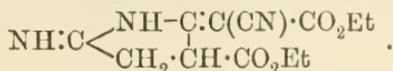
The preparation of this substance is described in a former paper (Part I of this series, *Trans.*, 1904, **85**, 1736), but, as since that time it has been found more convenient to employ a slightly modified method for the preparation of it in quantity, and as, moreover, the analysis given in the reference cited above referred to another compound which had been prepared in a concurrent research and had been included by an oversight, it is desirable to give the improved method of preparation and the correct analysis in the present instance. One hundred and thirteen grams of ethyl cyanoacetate are mixed with a solution of 11.5 grams of sodium dissolved in 122 grams of alcohol, and the mixture heated on the water-bath until a clear solution is obtained, that is to say, for about two hours. Water is then added, and the solution, after being rendered faintly acid by means of acetic acid, is distilled in a current of steam until the distillate ceases to give an acid reaction. The crude imino-ester, which solidifies in the flask on cooling, is then collected and is sufficiently pure for further use, although for the purpose of obtaining a dry specimen the product is best extracted by means of ether and the ethereal extract dried and evaporated. The following analyses are those which should have been given in the former paper, in which the formula $\text{C}_{10}\text{H}_{14}\text{O}_4\text{N}_2$ should read $\text{C}_{11}\text{H}_{14}\text{O}_4\text{N}_2$:

0.1923 gave 0.3739 CO₂ and 0.1090 H₂O. C=53.01; H=6.3.

0.2041 ,, 21.5 c.c. N₂ at 15° and 770 mm. N=12.5.

C₁₀H₁₄O₄N₂ requires C=53.1; H=6.2; N=12.4 per cent.

Ethyl 2-Imino-4-carbethoxytetrahydropyrrolidene-5-cyanoacetate,



This substance is prepared by the condensation of iodoacetonitrile with the sodium compound of ethyl β -imino- α -cyanoglutarate. Iodoacetonitrile has been prepared by Henry (*Bull. Soc. chim.*, 1887, [ii], 47, 400) and by Scholl (*Ber.*, 1896, 29, 2416) by the action of potassium iodide on chloroacetonitrile, whilst an improved method for its preparation has been recently given by v. Braun (*Ber.*, 1908, 41, 2134). For our purpose, it was found more convenient to use Scholl's method, mainly because ethyl chloroacetate was ready to hand. We are, however, quite in agreement with v. Braun's observation that to employ the entire method of Scholl, which involves the purification of the product by distillation in a current of steam, is fatal to the production of anything like a good yield, as the idonitrile is for the most part hydrolysed to the amide by this process. In the preparation of this substance by Scholl's process, we therefore avoided the use of water as far as possible, the alcoholic solution obtained after treating chloroacetonitrile with potassium iodide being evaporated as far as possible to free it from alcohol and then extracted by ether. It is necessary to wash the ethereal extract with water in order to free it from the last traces of alcohol, but this process does not affect the yield of the nitrile.

The condensation of iodoacetonitrile and the sodium compound of ethyl β -imino- α -cyanoglutarate is best effected in the following way. 2.4 Grams of sodium are dissolved in 50 grams of alcohol and added to a solution of 23 grams of ethyl β -imino- α -cyanoglutarate dissolved in its own volume of alcohol. The alcoholic solution containing the sodium compound of the imino-nitrile is then cautiously mixed with 17 grams of iodoacetonitrile, when a vigorous reaction ensues, and it is necessary to keep the reacting mixture cool by means of running water. Soon after the first addition of iodoacetonitrile, the condensation product begins to separate as a yellow, crystalline precipitate, and when all has been added, and the heat of the reaction has subsided, the separation is almost complete. It is best, however, to keep the product for half an hour, when water is added, and the imino-ester collected. It is best purified by rubbing with cold absolute alcohol, in which

it is practically insoluble, and is then sufficiently pure for further use. A specimen was prepared for analysis by recrystallisation from a large quantity of alcohol, from which solvent it separates in small, pale yellow needles, melting and decomposing at 205°:

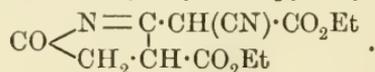
0.1850 gave 0.3686 CO₂ and 0.0967 H₂O. C=54.34; H=5.81.

0.2008 ,, 26.4 c.c. N₂ at 11° and 750 mm. N=15.5.

C₁₂H₁₅O₄N₃ requires C=54.3; H=5.7; N=15.8 per cent.

Ethyl 2-imino-4-carbethoxytetrahydropyrrolidene-5-cyanoacetate is sparingly soluble in all the usual organic solvents. It is insoluble in alkali carbonate solutions even on boiling, but is slowly soluble in aqueous alkali hydroxides. The alkaline solution thus formed precipitates the original compound, melting at 205° on being rendered acid with acetic acid, and when shaken in the air passes into a deep blue compound, the nature of which has not as yet been determined. The imino-nitrile dissolves at once in concentrated hydrochloric acid, evidently without undergoing any considerable change, as the original base is, for the most part, reprecipitated on adding water; a small quantity of the oxygen derivative (see below) is, however, also formed at the same time owing to the hydrolysis of the imino-form of the base, the quantity being increased if the action of the acid is prolonged. The concentrated hydrochloric acid solution yields a crystalline precipitate on standing, which is evidently the *hydrochloride* of the amino-form, since, on treatment with water, it is reconverted into the base, decomposing at 205°. It was not found possible, however, to contain a satisfactory analysis of this salt, owing to the fact that it rapidly lost hydrogen chloride on drying, even in a desiccator at the ordinary temperature.

Ethyl 2-Keto-4-carbethoxydihydroisopyrrolyl-5-cyanoacetate,



This is the *isopyrrole* form of the ketone derived from the above imino-nitrile, and can be prepared from it either by the action of nitrous acid or by hydrolysis with dilute hydrochloric acid. As the former method always yields a dark coloured product which is difficult to purify, the action of hydrochloric acid is most to be recommended for its preparation. The method found most suitable was the following. Five grams of the imino-nitrile were dissolved in sufficient concentrated hydrochloric acid, and the clear solution poured into five times its volume of boiling water. A clear solution was obtained, which, after the lapse of a few minutes, became cloudy, owing to the separation of the ketone in the form

of an oil. The hydrolysis was found to be complete after five minutes, when the solution was cooled and the oil allowed to crystallise. The compound separated from dilute alcohol in long, colourless needles, melting at 109°:

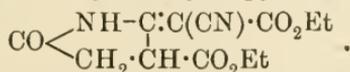
0.1766 gave 0.3524 CO₂ and 0.0793 H₂O. C=54.42; H=4.99.

0.2026 ,, 18.6 c.c. N₂ at 17° and 760 mm. N=10.6.

C₁₂H₁₄O₅N₂ requires C=54.1; H=5.3; N=10.5 per cent.

The production of the ketone by this process is almost quantitative, and no trace of other products could be detected. *Ethyl 2-keto-4-carbethoxydihydropyrrolyl-5-cyanoacetate* is insoluble in ice-cold aqueous sodium carbonate, but dissolves on warming, forming the sodium salt of the pyrrole modification (see below). The alkaline solution can be boiled for a considerable time without effecting any change, ultimately, however, hydrolysis ensues, and open-chain degradation products are formed. It is instantly soluble in aqueous alkali hydroxides, forming a solution which slowly oxidises to a blue compound on shaking with air, and is characterised by giving a substance closely resembling indigo in appearance when it is boiled for a short time with methyl sulphate. This compound, as well as that which is formed from it on oxidation, are under investigation. The keto-ester does not lend itself to the formation of derivatives, and is unacted on by semi-carbazide and by aniline. It may also be prepared from the imino-compound by the action of nitrous acid, but the product formed in this manner is always dark coloured and difficult to purify; the formation in this way shows, however, that the imino-compound reacts in the amino-form, since the reaction is carried out in acetic acid solution, which does not hydrolyse the imino-form. The formation of derivatives of glutazine from the keto-ester by the action of dilute sulphuric acid is described on page 1526.

Ethyl 2-Keto-4-carbethoxytetrahydropyrrolidene-5-cyanoacetate,



The above pyrrole form of the ketone can be prepared by gently warming 3 grams of the *isopyrrole* form with aqueous sodium carbonate solution until all has passed into solution, and then, after cooling the solution with ice, cautiously acidifying it with hydrochloric acid. A small quantity of the *isopyrrole* form first separates as an oil, which can be removed by filtration, and the filtrate then gives a white, crystalline precipitate on scratching the sides of the containing vessel. The compound prepared in this

way melts at 129° , and dissolves in aqueous sodium carbonate solution with effervescence. It cannot be recrystallised, since at a comparatively low temperature the *isopyrrole* modification is regenerated. Its purity was tested by again dissolving the product, melting at 129° , in sodium carbonate solution, and reprecipitating with hydrochloric acid in the manner described above, when the melting point of the acid was found to be unaltered:

0.1818 gave 0.3592 CO_2 and 0.0832 H_2O . $\text{C}=53.88$; $\text{H}=5.08$.

$\text{C}_{12}\text{H}_{14}\text{O}_5\text{N}_2$ requires $\text{C}=54.1$; $\text{H}=5.3$ per cent.

The pyrrole form appears to be more soluble in water than the *isopyrrole* form, but is much less soluble in alcohol. The acid gave the following figures on titration: 0.2962 requires 11.4 c.c. of *N*/10-sodium hydroxide: a monobasic acid, $\text{C}_{12}\text{H}_{14}\text{O}_5\text{N}_2$, requires 11.5 c.c.

The *silver* salt, $\text{C}_{12}\text{H}_{13}\text{O}_5\text{N}_2\text{Ag}$, is a gelatinous substance, which can, however, be dried at 80° without undergoing change:

0.2276 gave 0.0659 Ag. $\text{Ag}=28.95$.

$\text{C}_{12}\text{H}_{13}\text{O}_5\text{N}_2\text{Ag}$ requires $\text{Ag}=28.95$ per cent.

Conversion of Ethyl 2-Keto-4-carbethoxyppyrrolidene-5-cyanoacetate into Ethyl 2-Keto-4-carbethoxydihydroisopyrrolyl-5-cyanoacetate.—This conversion is completely effected when the first-named compound is melted. It can, however, be conveniently brought about by dissolving the pyrrole form in hot alcohol, when the *isopyrrole* modification separates from the solution on cooling. For the purpose of converting larger quantities, the following method yields good results. Ten grams of the pyrrole form are mixed with 100 c.c. of boiling water, and the clear solution allowed to cool. An oil separates, which quickly sets to a viscid syrup, and can be removed by the aid of a glass rod, leaving a solution which can be filtered if necessary, and deposits a small quantity of unchanged pyrrole form on standing. The viscid syrup collected on the glass rod rapidly solidifies on rubbing with water, and when recrystallised from dilute alcohol yields the characteristic needles of the *isopyrrole* modification, melting at 109° . It is possible, by boiling the aqueous solution of the pyrrole form for a longer period of time, to convert it completely into the *isopyrrole* modification.

The Products of Alkaline Hydrolysis of Ethyl 2-Keto-4-carbethoxy-dihydroisopyrrolyl-5-cyanoacetate.

(1) *Ethyl Dihydrogen β -Imino- α -cyanobutane- α - γ -tricarboxylate,*
 $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{C}(\text{:NH})\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}.$

This compound occurs as an intermediate product in the hydrolysis of the isopyrrole derivative by means of aqueous sodium carbonate, which leads ultimately to the formation of ethyl hydrogen α -cyano- β -keto adipate (see below), and can be isolated by extracting the mother liquors from this substance by means of ether. It may be, however, prepared in larger quantity by the hydrolysis of the imino-compound by the following process. Ten grams of ethyl 2-imino-4-carbethoxytetrahydropyrrolidene-5-cyanoacetate are mixed with 50 c.c. of boiling water and 10 c.c. of 50 per cent. aqueous potassium hydroxide added. The clear solution is then shaken until a test portion no longer gives a precipitate with hydrochloric acid, which occurs after about five minutes, when the solution is acidified and extracted thoroughly with ether. When purified by recrystallisation from dilute hydrochloric acid (1:1), the ethyl hydrogen salt is obtained in small, colourless prisms, melting at 160° , evolving carbon dioxide, and almost immediately resolidifying to a yellow solid (the lactam of carbethoxyglutazylacetic acid: see page 1526):

0.1830 gave 0.3134 CO_2 and 0.0793 H_2O . C=46.70; H=4.81.

$\text{C}_{10}\text{H}_{12}\text{O}_6\text{N}_2$ requires C=46.9; H=4.7 per cent.

The acid is fairly readily soluble in cold water, and when warmed with aqueous potassium hydroxide evolves ammonia and passes into ethyl hydrogen α -cyano- β -keto adipate (see below). The *silver* salt, $\text{C}_{10}\text{H}_{10}\text{O}_6\text{N}_2\text{Ag}_2$, is precipitated as a white, crystalline solid on adding the calculated quantity of a solution of silver nitrate to a neutral solution of the ammonium salt of the acid:

0.2109 gave 0.0968 Ag. Ag=45.89.

$\text{C}_{10}\text{H}_{10}\text{O}_6\text{N}_2\text{Ag}_2$ requires Ag=45.95 per cent.

(2) *Ethyl Hydrogen α -Cyano- β -keto adipate,*
 $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}.$

This ketone is the final product of the action of boiling sodium carbonate solution on ethyl 2-keto-4-carbethoxytetrahydropyrrolidene-5-cyanoacetate or its isomeride, and can be prepared in quantity by the following process. Ten grams of the pyrrole or isopyrrole derivative are mixed with 100 c.c. of a 10 per cent. solution of sodium carbonate, and boiled until the odour of

ammonia ceases to be apparent, an operation which takes about six hours. The clear solution is then acidified with hydrochloric acid, causing the separation of an oil which rapidly solidifies. It can be purified by recrystallisation from dilute alcohol, when it yields colourless needles melting at 104° , and evolving gas at 140° :

0.1957 gave 0.3626 CO_2 and 0.0933 H_2O . C=50.53; H=5.29.

0.2660 ,, 15.4 c.c. N_2 at 17° and 762 mm. N=6.73.

$\text{C}_9\text{H}_{11}\text{O}_5\text{N}$ requires C=50.7; H=5.1; N=6.6 per cent.

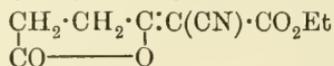
Ethyl hydrogen α -cyano- β -keto adipate is readily soluble in all the usual organic solvents excepting light petroleum. It gives in alcoholic solution a deep red colour with ferric chloride. It was proved to be a dibasic acid by titration with *N*/10-sodium carbonate.

The *silver* salt, $\text{C}_9\text{H}_9\text{O}_5\text{NAg}_2$, separates as a white, crystalline solid on adding the calculated quantity of a solution of silver nitrate is a neutral solution of the ammonium salt of the acid:

0.2463 gave 0.1246 Ag. Ag=50.58.

$\text{C}_9\text{H}_9\text{O}_5\text{NAg}_2$ requires Ag=50.58 per cent.

Lactone of Ethyl Hydrogen α -Cyano- β -hydroxy- α - β -hydromuconate,



This substance can be prepared by the distillation of ethyl hydrogen α -cyano- β -keto adipate. The following conditions were employed. Five grams of the ketone were placed in a small distillation flask fitted to the vacuum distillation apparatus, and heated under diminished pressure until all water had been evolved, when the residue was distilled, and the fraction boiling at $140\text{--}150^{\circ}/30$ mm. collected. The colourless oil obtained in this way partly solidified on keeping, and the mixture was therefore treated with sodium carbonate solution, in which the solid dissolved, leaving the oil unchanged. The oil was then separated by means of ether, the ethereal solution leaving an oil on evaporation which boiled at $142\text{--}145^{\circ}/30$ mm., yielding a clear, fairly mobile liquid which could not be crystallised:

0.2145 gave 13.8 c.c. N_2 at 20° and 751 mm. N=7.3.

$\text{C}_9\text{H}_9\text{O}_4\text{N}$ requires N=7.2 per cent.

The lactone is insoluble in cold water and only slowly dissolves on boiling, separating for the most part unchanged from the solution on cooling. It can be distilled in a current of steam without undergoing appreciable hydrolysis, but is quickly hydrolysed by hot aqueous alkali hydroxide, yielding a clear solution, from which ethyl hydrogen α -cyano- β -keto adipate separates on

acidifying. The sodium carbonate solution obtained in the purification of the lactone yields a solid acid on acidifying, which separates from benzene in colourless plates melting at 121° . It gives no colour with ferric chloride, and does not decolorise permanganate in sodium hydrogen carbonate solution. The quantity obtained was too small for further investigation.

(3) *Succinic and Malonic Acids.*

The ultimate products obtained by the complete hydrolysis of ethyl 2-keto-4-carbethoxydihydroisopyrrolyl-5-cyanoacetate with aqueous potassium hydroxide are succinic and malonic acids. The experimental conditions employed were as follows. Five grams of the isopyrrole derivative were suspended in water and mixed with aqueous potassium hydroxide containing one and a-half times the calculated quantity of the alkali. The solution was then boiled until ammonia ceased to be evolved, when hydrochloric acid was added, and the clear solution extracted on the shaking machine with ether. The ethereal solution on evaporation left a solid residue, which, when recrystallised from water, yielded the characteristic crystals of succinic acid melting at 185° :

0.1810 gave 0.2706 CO_2 and 0.0844 H_2O . C=40.77; H=5.18.

$\text{C}_4\text{H}_6\text{O}_4$ requires C=40.7; H=5.1 per cent.

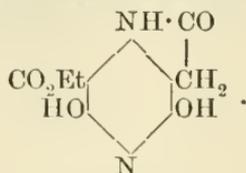
The aqueous residue from the ether extraction was then evaporated to dryness on the water-bath, and the dry residue extracted in a Soxhlet apparatus with ether. The ethereal extract on evaporation yielded a solid residue containing a considerable quantity of succinic acid, which had not been extracted in the previous extraction. The separation was effected by rubbing the mixed acids with dry ether, in which succinic acid is practically insoluble, but in which malonic acid dissolves readily. By repeating the process, it was ultimately possible to isolate malonic acid, melting at 132° :

0.1938 gave 0.2439 CO_2 and 0.0675 H_2O . C=34.31; H=3.87.

$\text{C}_3\text{H}_4\text{O}_4$ requires C=34.6; H=3.8 per cent.

The Products of Acid Hydrolysis of Ethyl 2-Keto-4-carbethoxy-dihydroisopyrrol-5-cyanoacetate.

(1) *The Lactam of Carbethoxyglutazylacetic Acid,*



This substance may be prepared either by the action of dilute sulphuric acid on the *isopyrrole* derivative, or by heating ethyl dihydrogen β -imino- α -cyanobutane- $\alpha\gamma\delta$ -tricarboxylate above its melting point.

(i) *From the isopyrrole derivative.*—This method, which is the most convenient for the preparation of large quantities of the lactam, is carried out as follows. Ten grams are boiled with a 10 per cent. solution of sulphuric acid until the oil which floats at the top of the hot acid has completely solidified, when the solid is collected and separated from any unchanged *isopyrrole* derivative by washing with alcohol.

(ii) *From the dihydrogen salt.*—Five grams are heated in a test-tube placed in a bath of sulphuric acid at 155° for ten minutes. Some carbon dioxide is evolved during the process of heating, and the solid ultimately becomes transformed into a yellow, semi-solid mass. It is then cooled and mixed with dilute sodium carbonate solution, which causes the oily portion to dissolve, leaving a yellow solid; this can be obtained colourless by washing with alcohol. The sodium carbonate solution, on acidifying, yields an oil, which becomes solid on scratching, and consists of ethyl hydrogen β -imino- α -cyanoadipate,



melting at 131° (see page 1534), which is evidently formed by the elimination of the carboxyl group from the dihydrogen salt.

When prepared by either of these methods, the lactam is an insoluble substance, which separates from a large quantity of hot water as small needles, decomposing at a high temperature without melting:

0.1863 gave 0.3441 CO_2 and 0.0705 H_2O . C=50.37; H=4.20.

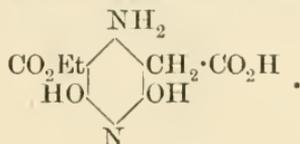
0.2010 ,, 20.1 c.c. N_2 at 9° and 757 mm. N=11.9.

$\text{C}_{10}\text{H}_{10}\text{O}_5\text{N}_2$ requires C=50.4; H=4.2; N=11.8 per cent.

The lactam is insoluble in cold sodium carbonate solution, and

its aqueous solution gives a purple coloration with ferric chloride, which changes to green after boiling for a few minutes.

(2) *Carbethoxyglutazylacetic Acid*,



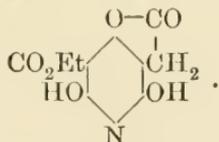
The lactam described above dissolves when boiled with sodium carbonate solution, and the above acid separates when the cold alkaline solution is acidified. The compound does not possess a definite melting point, and cannot be recrystallised, since when boiled with water it is reconverted into the lactam, which separates from the solution on cooling:

0.2012 gave 18.2 c.c. N_2 at 10° and 758 mm. $\text{N} = 10.8$.

$\text{C}_{10}\text{H}_{12}\text{O}_6\text{N}_2$ requires $\text{N} = 10.9$ per cent.

The acid is soluble in sodium carbonate solution, and behaves towards ferric chloride in the same manner as the lactam.

(3) *The Lactone of Trihydroxycarbethoxypyridylacetic Acid*,



This compound can be prepared by the action of nitrous acid on carbethoxyglutazylacetic acid in the following way. The glutazine derivative is dissolved in dilute aqueous potassium hydroxide, and, after having been mixed with a solution containing excess of sodium nitrite, is poured into a hot dilute solution containing excess of acetic acid. The mixture becomes at once deep green, and the pyridine derivative slowly separates as a crystalline powder. It was purified by recrystallisation from water, in which it is sparingly soluble, and obtained in microscopic needles, which decompose at a high temperature without melting:

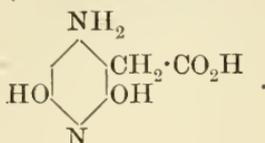
0.1913 gave 0.3513 CO_2 and 0.0671 H_2O . $\text{C} = 50.08$; $\text{H} = 3.89$.

$\text{C}_{10}\text{H}_9\text{O}_6\text{N}$ requires $\text{C} = 50.2$; $\text{H} = 3.8$ per cent.

The lactone is insoluble in sodium carbonate solution, and gives in aqueous solution a red coloration with ferric chloride, which disappears on warming. The corresponding acid could not be isolated, for, although the lactone dissolved when boiled with sodium carbonate solution, evidently undergoing transformation

into the sodium salt of the acid, yet on acidifying the solution a substance separated which was insoluble in sodium carbonate solution, and was evidently therefore the lactone.

(4) *Glutazylacetic Acid*,



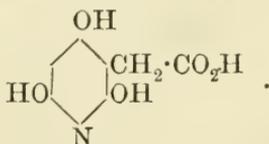
This acid can be prepared by the action of aqueous potassium hydroxide on the lactam of carbethoxyglutazylacetic acid. The lactam is mixed with 30 per cent. aqueous potassium hydroxide, and the solution boiled in an open vessel until the odour of ammonia begins to be apparent. Water is then added, and the solution acidified with hydrochloric acid. Providing the solution is sufficiently concentrated, the acid then slowly separates as a crystalline precipitate; this can be purified by recrystallisation from a little water, from which it separates in small, glistening plates, usually pale yellow in colour. The acid melts and blackens at about 270° when rapidly heated, but when slowly heated begins to char much below this temperature:

0.2121 gave 28.6 c.c. N_2 at 17° and 748 mm. $\text{N} = 15.4$.

$\text{C}_7\text{H}_8\text{O}_4\text{N}_2$ requires $\text{N} = 15.2$ per cent.

Glutazylacetic acid is readily soluble in hot water. It gives with ferric chloride in aqueous solution a red coloration, which changes to green on boiling. The acid does not appear to pass readily into the lactam, for, although it evidently loses water on heating, yet at the high temperature necessary much charring takes place, and no definite product could be isolated.

(5) *Trihydroxypyridylacetic Acid*,



This acid may be prepared either by the hydrolysis of trihydroxycarbethoxypyridylacetic acid with potassium hydroxide, or by the action of dilute sulphuric acid on glutazylacetic acid.

(1) *From trihydroxycarbethoxypyridylacetic acid*.—Three grams of the acid are heated in an open vessel with 5 c.c. of 30 per cent. aqueous potassium hydroxide until a test portion gives no precipitate on acidifying. The solution is then acidified with

hydrochloric acid and kept, when, provided the solution is sufficiently concentrated, the pyridine acid slowly separates as a crystalline powder.

(2) *From glutazylacetic acid.*—Three grams of the acid are boiled with 10 per cent. sulphuric acid for two hours. The solution is then rendered alkaline with ammonia, acidified with hydrochloric acid, and evaporated on the water-bath to a small bulk. The pyridine derivative separates on keeping the concentrated solution.

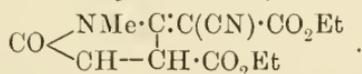
Trihydroxypyridylacetic acid separates from a small amount of water in small prisms, usually yellow in colour. It does not possess a definite melting point, but when heated begins to blacken at about 220°:

0.2182 gave 14.4 c.c. N₂ at 18° and 763 mm. N=7.7.

C₇H₇O₅N requires N=7.6 per cent.

The acid is readily soluble in water, and gives a red coloration with ferric chloride, which disappears on warming. As in the case of glutazylacetic acid, the corresponding anhydride could not be isolated owing to the high temperature required for its formation.

Ethyl 2-Keto-4-carbethoxy-1-methyltetrahydropyrrolidene-5-cyanoacetate,



The methylation of ethyl 2-keto-4-carbethoxytetrahydropyrrolidene-5-cyanoacetate cannot be readily effected. The substance is a strong acid, but acid etherifying agents, such as alcohol and sulphuric acid, cannot be used, since at the necessary temperature the compound rearranges to the *isopyrrole* form, which does not alkylate. Moreover, alkaline alkylating agents, such as sodium ethoxide and an alkyl iodide, do not lead to good results, as the sodium salt of the pyrrole form is not readily acted on by alkyl iodides. The only satisfactory method is to treat the silver salt suspended in dry benzene with methyl iodide in the following manner. Five grams of the silver salt, prepared in the way described on page 1522, were carefully dried at 80°, ground to a fine powder, and transferred to a Geissler flask, in which it was mixed with 50 c.c. of dry benzene. Excess of methyl iodide was then added, and the flask heated on the water-bath. The reaction commenced on warming, and was complete after heating for two hours, when the benzene solution was filtered and evaporated. The oily residue solidified on cooling, and was purified by recrystallisation from alcohol, being obtained in long, colourless needles, melting at 84°:

0.1859 gave 0.3791 CO₂ and 0.0950 H₂O. C = 55.62; H = 5.67.

C₁₃H₁₆O₅N₂ requires C = 55.7; H = 5.7 per cent.

The methyl derivative is insoluble in cold aqueous potassium hydroxide. A small quantity of the same methyl derivative was obtained on alkylating the pyrrole derivative by means of sodium ethoxide and methyl iodide.

Hydrolysis of Ethyl 2-Keto-4-carbethoxy-1-methyltetrahydropyrrolidene-5-cyanoacetate.—This hydrolysis is best effected by means of aqueous potassium hydroxide under conditions which allow the methylamine formed to be collected. Five grams were placed in a flask connected with a condenser and mixed with an aqueous solution containing the calculated quantity of potassium hydroxide necessary to hydrolyse it to the dipotassium salt of ethyl hydrogen α -cyano- β -keto adipate,



that is to say, 4 grams. The flask was then heated on the sand-bath, and the distillate collected in dilute hydrochloric acid, care being taken to prevent loss of methylamine by causing the condenser tube to dip under the surface of the acid. The heating was continued until all oil had passed into solution, when steam was passed through the flask in order to remove the last traces of the base. The residue was then acidified, yielding an oil which solidified on standing. It was collected and recrystallised from dilute alcohol, giving colourless needles, melting at 104°, which analysis showed to consist of ethyl hydrogen α -cyano- β -keto adipate:

0.1805 gave 0.3347 CO₂ and 0.0809 H₂O. C = 50.52; H = 4.98.

C₉H₁₁O₅N requires C = 50.7; H = 5.1 per cent.

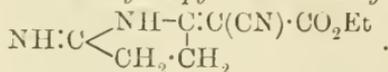
The hydrochloric acid distillate was then evaporated to a small bulk, and mixed with excess of platinic chloride solution and an equal volume of alcohol. The golden-yellow plates which then separated were collected, dried, and analysed:

0.2316 gave 0.0954 Pt. Pt = 41.19.

(NH₂Me, HCl)₂PtCl₄ requires Pt = 41.34 per cent.

The base was therefore methylamine.

Ethyl 2-Iminotetrahydropyrrolidene-5-cyanoacetate,



The carbethoxy-group can be readily eliminated from ethyl 2-imino-4-carbethoxytetrahydropyrrolidene-5-cyanoacetate without affecting the imino-group by the following process. Ten grams of the imino-ester, ground to a fine powder, are suspended in 100 c.c. of water at 80° and mixed with 20 c.c. of 50 per cent.

aqueous potassium hydroxide. A clear solution is at once obtained, which is kept for thirty seconds and is then quickly cooled. It is advisable to avoid shaking the flask during this period, as the alkaline solution rapidly oxidises to a blue compound when in contact with air. The cooled solution is then acidified with acetic acid, and a quantity of unaltered imino-compound which then separates is collected. It is possible so to arrange the time of the reaction as to cause the whole of the carbethoxy-derivative to be hydrolysed by the alkali, in which circumstances none is, of course, recovered on acidifying with acetic acid. This point is, however, difficult to determine, and as other products are formed by the further action of the alkali, it is best to use the above conditions, which enable the reaction to be stopped before the whole of the carbethoxy-derivative is hydrolysed. The recovered ester can, of course, be used again. The filtrate from the unaltered imino-compound which contains the carboxylic acid in solution is then boiled, whereby carbon dioxide is eliminated, and ethyl 2-iminotetrahydropyrrolidene-5-cyanoacetate precipitated. When recrystallised from a large volume of alcohol, it is obtained in microscopic needles, usually pale yellow in colour, which melt and decompose at 256° :

0.1610 gave 0.3319 CO_2 and 0.0802 H_2O . C=56.22; H=5.53.

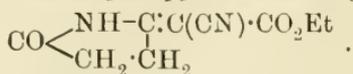
0.2006 ,, 37.2 c.c. N_2 at 15° and 762 mm. N=21.77.

$\text{C}_9\text{H}_{11}\text{O}_2\text{N}_3$ requires C=55.9; H=5.7; N=21.7 per cent.

Ethyl 2-iminotetrahydropyrrolidene-5-cyanoacetate is sparingly soluble in all the usual organic solvents, but can be recrystallised from a large volume of hot water, in which it is more soluble than the corresponding carbethoxy-derivative. It is quite insoluble in alkali carbonates or hydroxides, but in the case of the last-named reagents it dissolves on warming, yielding products of fission of the pyrrolidine ring. It is obtained by the process given above in yields of about 75 per cent. of the theoretical, although this is considerably decreased if the action of the alkali is prolonged, for by this means the pyrrolidine ring is broken and ethyl hydrogen β -imino- α -cyanoadipate,



(see page 1534), is formed. The imino-compound is soluble in dilute hydrochloric acid, but a crystalline hydrochloride could not be isolated.

Ethyl 2-Ketotetrahydropyrrolidene-5-cyanoacetate,

The above pyrrole form of the ketone may be prepared from the imino-compound by the action of dilute hydrochloric acid. Five grams of the imino-compound are finely ground and suspended in 30 c.c. of warm water. Five c.c. of concentrated hydrochloric acid are now added, and the clear solution kept, when long needles of the pyrrole form separate. It is best purified by rapid recrystallisation from alcohol, for, although a certain quantity is converted into the *isopyrrole* modification by this means, yet owing to the fact that the pyrrole form is much less soluble in alcohol than the *isopyrrole* form the crystals which separate first are pure *ethyl 2-ketotetrahydropyrrolidene-5-cyanoacetate*. The compound forms rhombic prisms, melting at 181°:

0.1822 gave 0.3716 CO₂ and 0.0838 H₂O. C=55.62; H=5.11.

0.2120 „ 26.4 c.c. N₂ at 17.5° and 748 mm. N=14.2.

C₉H₁₀O₃N₂ requires C=55.7; H=5.1; N=14.4 per cent.

The ethyl salt is characterised by forming alkali salts, which are insoluble in excess of the alkali. Thus, when treated with a concentrated solution of sodium carbonate, it dissolves, but almost directly deposits the *sodium* salt as a white, crystalline precipitate. In the same way, the potassium salt separates when the acid is dissolved in concentrated aqueous potassium hydroxide and allowed to stand.

The *potassium* salt, C₉H₈O₃N₂K, is best prepared by dissolving the acid in alcohol and adding an alcoholic solution containing the requisite quantity of potassium hydroxide, when it separates as a sandy powder. It can be conveniently purified by washing with hot alcohol, in which it is very sparingly soluble, but can also be recrystallised from a small quantity of water, from which solvent it separates in small, colourless prisms:

0.2278 gave 0.0844 K₂SO₄. K=16.61.

C₉H₈O₃N₂K requires K=16.88 per cent.

The salt is readily soluble in cold water, forming a solution which is alkaline to litmus.

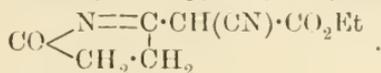
The *silver* salt, C₉H₈O₃N₂Ag, is difficult to prepare in the usual manner through the ammonium salt, but is readily formed when an aqueous solution of the potassium salt is mixed with a solution containing the calculated quantity of silver nitrate. It is a gelatinous substance, which can be dried to a fine, apparently amorphous powder by heating it at 80°:

0.2331 gave 0.0838 Ag. $\text{Ag} = 35.95$.

$\text{C}_9\text{H}_8\text{O}_3\text{N}_2\text{Ag}$ requires $\text{Ag} = 35.88$ per cent.

The silver salt is slowly affected on exposure to light.

Ethyl 2-Ketodihydroisopyrrolyl-5-cyanoacetate,



The *isopyrrole* form of the ketone can be prepared either by the action of nitrous acid on the imino-compound, or by the action of boiling dilute hydrochloric acid. In the first case, the pure *isopyrrole* derivative is formed, in the second a mixture of the two forms.

By the action of nitrous acid.—Ten grams of the imino-compound are ground to a fine powder and suspended in 20 c.c. of glacial acetic acid, the mixture being added to a boiling solution containing 5 grams of sodium nitrite in 100 c.c. of water. A considerable quantity of gas is evolved, and a clear solution, which is usually red in colour, is obtained after boiling for a few minutes. As soon as this point is reached, the solution is cooled, and the *isopyrrole* derivative which then separates is collected and purified by recrystallisation from either water or alcohol. It forms colourless needles, melting at 145° .

By the action of hot dilute hydrochloric acid.—The imino-compound is suspended in boiling water and concentrated hydrochloric acid added, the solution being raised to boiling for a few minutes. On cooling, crystals separate, which, when collected and treated with dilute sodium carbonate solution, leave an insoluble residue consisting of the *isopyrrole* form, melting at 145° . The sodium carbonate solution, on acidification, yields the pyrrole form, melting at 181° . The proportion of the two forms present in this product depends entirely on the length of time the hydrochloric acid solution is heated. It is possible, by prolonging the heating sufficiently, to obtain only the *isopyrrole* form, melting at 145° :

0.1778 gave 0.3630 CO_2 and 0.0818 H_2O . $\text{C} = 55.68$; $\text{H} = 5.11$.

0.2091 ,, 27.1 c.c. N_2 at 16.5° and 738 mm. $\text{N} = 14.6$.

$\text{C}_9\text{H}_{10}\text{O}_3\text{N}_2$ requires $\text{C} = 55.7$; $\text{H} = 5.1$; $\text{N} = 14.4$ per cent.

The *isopyrrole* derivative is insoluble in sodium carbonate solution, but dissolves on warming, being for the most part transformed, with fission of the *isopyrrole* ring, into the sodium salt of ethyl hydrogen β -imino- α -cyano adipate (see page 1534). It is soluble in cold aqueous potassium hydroxide, and, providing the alkali is strong, the potassium salt of the pyrrole form separates

on standing. The alkaline solution shows no tendency to oxidise in the air, and the action of methyl sulphate does not lead to the production of a coloured substance.

Transformation of the pyrrole form into the isopyrrole form, and vice versa.—The pyrrole form is comparatively stable, and it is possible to sublime it, when dry, at a temperature of 180° without causing it to pass into the isopyrrole modification. As already mentioned, it can be recrystallised from alcohol without undergoing change, although prolonged boiling with this solvent slowly converts it into the isopyrrole derivative. Hot water acts more quickly, and boiling for ten minutes is usually sufficient to convert one gram completely into the isopyrrole form. The reverse change is best effected through the potassium salt in the following way. One gram of the isopyrrole modification is dissolved in alcohol, and the requisite quantity of potassium hydroxide dissolved in alcohol added. The potassium salt of the pyrrole form separates, which, when dissolved in water and acidified, yields the pure pyrrole modification in glistening laminae, melting at 181° . The following analysis was made in order to establish its identity:

0.1797 gave 0.3662 CO_2 and 0.0834 H_2O . C=55.58; H=5.14.

$\text{C}_9\text{H}_{10}\text{O}_3\text{N}_2$ requires C=55.7; H=5.1 per cent.

Ethyl Hydrogen β -Imino- α -cyano adipate,
 $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}(\text{:NH})\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$.

This compound occurs in a number of reactions involving the hydrolysis of both ethyl 2-imino-4-carbethoxytetrahydropyrrolidene-5-cyanoacetate and ethyl 2-iminotetrahydropyrrolidene-5-cyanoacetate, but can be prepared in quantitative yield by warming ethyl 2-ketodihydroisopyrrolyl-5-cyanoacetate with sodium carbonate solution. The first action of the alkali is to form the sodium salt of the pyrrole modification, but if the solution is boiled for a few minutes fission of the pyrrole ring ensues with the production of the above compound. The operation is performed as follows. Two grams of the isopyrrole derivative or its isomeride are boiled with 20 c.c. of a 10 per cent. solution of sodium carbonate for five minutes, and the clear solution, after being cooled, is acidified with hydrochloric acid. A crystalline precipitate separates, which, when recrystallised from hot water, yields feathery needles, melting at 131° and evolving gas at 160° :

0.1786 gave 0.3331 CO_2 and 0.0906 H_2O . C=50.86; H=5.63.

0.2040 ,, 23 c.c. N_2 at 12.5° and 747 mm. N=13.37.

$\text{C}_9\text{H}_{12}\text{O}_4\text{N}_2$ requires C=50.9; H=5.7; N=13.2 per cent,

The *silver* salt, $C_9H_{11}O_4N_2Ag$, separates as a white, bulky precipitate when the calculated quantity of an aqueous solution of silver nitrate is added to a neutral solution of the ammonium salt of the acid. It darkens rapidly on exposure to light:

0.2173 gave 0.0735 Ag. $Ag = 33.82$.

$C_9H_{11}O_4N_2Ag$ requires $Ag = 33.85$ per cent.

Ethyl hydrogen β -imino- α -cyano adipate is stable towards hot sodium carbonate solution, and can be boiled for some time with this reagent without undergoing change, but, when boiled for a few minutes with aqueous potassium hydroxide, it evolves ammonia and passes into ethyl hydrogen α -cyano- β -keto adipate (see page 1524). The operation is effected by boiling 1 gram with 5 c.c. of a 20 per cent. solution of potassium hydroxide for one minute and acidifying the solution, when an oil separates which slowly solidifies. On recrystallisation from dilute alcohol, it yields the characteristic needles of ethyl hydrogen α -cyano- β -keto adipate, melting at 104° , and giving a red coloration with ferric chloride:

0.2454 gave 14.2 c.c. N_2 at 18° and 762 mm. $N = 6.7$.

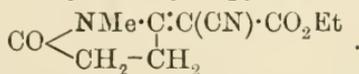
$C_9H_{11}O_5N$ requires $N = 6.6$ per cent.

Ethyl hydrogen β -imino- α -cyano adipate is slowly hydrolysed by mineral acids to the corresponding ketone, and is partly transformed into the same compound on treatment with nitrous acid. When distilled rapidly, in small quantities, under the ordinary pressure, it loses water and is reconverted into ethyl 2-ketodihydroisopyrrolyl-5-cyanoacetate. The following analysis was made of the product obtained in this way and recrystallised from water. It melted at 145° :

0.2300 gave 29.8 c.c. N_2 at 17° and 740 mm. $N = 14.6$.

$C_9H_{10}O_3N_2$ requires $N = 14.4$ per cent.

Ethyl 2-Keto-1-methyltetrahydropyrrolidene-5-cyanoacetate,



The methylation of ethyl 2-ketotetrahydropyrrolidene-5-cyanoacetate presented some difficulties. In the first place, it was not found possible to bring about interaction between the potassium salt and methyl iodide, for even after prolonged boiling in alcoholic solution the potassium salt remained unacted on. Again, when the potassium salt was suspended in methyl alcohol and treated with methyl sulphate, although interaction ensued and potassium sulphate separated, the product was found to consist of unchanged ethyl 2-ketotetrahydropyrrolidene-5-cyanoacetate, and no trace of a methyl derivative could be isolated. This curious

reaction is evidently caused by the ionisation of the potassium salt in solution. Attempts made to prepare the methyl derivative by the ordinary process of alcohol and sulphuric acid etherification led to no result, since at the necessary temperature the pyrrole form was completely converted into the *isopyrrole* form, which is unacted on by these reagents. Finally, the desired result was obtained by methylating the compound through the silver salt. Five grams of the silver salt were prepared from the potassium salt in the manner described on page 1532, and after being carefully dried in an air-oven at 80° the salt was transferred to a flask fitted with a reflux condenser, in which it was mixed with 100 c.c. of carefully dried benzene containing excess of methyl iodide. The flask was then heated on the water-bath for two hours, at the end of which time the greater portion of the silver salt had been decomposed. The benzene solution was then filtered and evaporated, leaving an oily residue, which rapidly solidified. When recrystallised from alcohol, it formed colourless prisms melting at 120°:

0.1802 gave 0.3799 CO₂ and 0.0940 H₂O. C=57.49; H=5.79.

C₁₀H₁₂O₃N₂ requires C=57.7; H=5.8 per cent.

The methyl derivative is insoluble in cold aqueous potassium hydroxide.

Ethyl Hydrogen α-Cyano-β-methyliminoadipate,
CO₂H·CH₂·CH₂·C(:NMe)·CH(CN)·CO₂Et.

This substance is formed by the hydrolysis of ethyl 2-keto-1-methyltetrahydropyrrolidene-5-cyanoacetate by means of sodium carbonate solution in the following way. Five grams of the pyrrole derivative are mixed with 20 c.c. of a 10 per cent. solution of sodium carbonate, and boiled until all has passed into solution and no separation of oil takes place on cooling. The cold solution is then acidified with hydrochloric acid, and the crystalline precipitate which separates is purified by recrystallisation from water. When rapidly crystallised from this solvent, it forms lustrous plates, but when allowed to separate slowly it is obtained in long, slender needles. It melts at 155°, and gives off gas when heated to a high temperature:

0.1973 gave 0.3835 CO₂ and 0.1120 H₂O. C=53.02; H=6.31.

C₁₀H₁₄O₄N₂ requires C=53.1; H=6.2 per cent.

The *silver* salt, C₁₀H₁₃O₄N₂Ag, separates as a white, crystalline precipitate when the calculated quantity of silver nitrate solution is added to a neutral solution of the ammonium salt:

0.2541 gave 0.0821 Ag. Ag=32.31.

$C_{10}H_{13}O_4N_2Ag$ requires Ag=32.43 per cent.

Ethyl hydrogen α -cyano- β -methyliminoadipate is reconverted into ethyl 2-keto-1-methyltetrahydropyrrolidene-5-cyanoacetate on rapid distillation under the ordinary pressure. The following analysis was made of the product obtained in this way, which melted at 120° :

0.2248 gave 24.1 c.c. N_2 at 12° and 750 mm. N=12.6.

$C_{10}H_{14}O_4N_2$ requires N=12.4 per cent.

The formation of methylamine and ethyl hydrogen α -cyano- β -ketoadipate from ethyl hydrogen α -cyano- β -methyliminoadipate.—This transformation was effected by the action of potassium hydroxide solution in the following way. Five grams of the imino-compound were heated under the same conditions as described on page 1530 for ten minutes, when steam was passed through the flask, and the contents were finally cooled and acidified. The oil which separated solidified on keeping, and on recrystallisation from dilute alcohol yielded the characteristic crystals of ethyl hydrogen α -cyano- β -ketoadipate, melting at 104° , and giving a red coloration with ferric chloride:

0.2401 gave 13.9 c.c. N_2 at 18° and 761 mm. N=6.7.

$C_9H_{11}O_5N$ requires N=6.6 per cent.

The hydrochloric acid distillate was evaporated to a small bulk, mixed with platinic chloride solution, and then with an equal volume of alcohol. The yellow platinum salt which then separated was collected and analysed:

0.2328 gave 0.0957 Pt. Pt=41.10.

$(NH_2Me, HCl)_2PtCl_4$ requires Pt=41.34 per cent.

The base was evidently therefore methylamine.

Much of the expense entailed by this research has been met by grants from the Government Grant Committee of the Royal Society and from the Research Fund of the Chemical Society, for which we desire to express our indebtedness.

UNIVERSITY,
MANCHESTER.

CLXXIII.—*Halogen Derivatives of Cinnamic Acid.*

By THOMAS CAMPBELL JAMES and JOHN JOSEPH SUDBOROUGH.

A.—*Attempted Resolution of α -Bromocinnamic Acids by means of Strychnine.*

As a rule an unsaturated acid of the type $R\cdot CH:CH\cdot CO_2H$ exists in two well defined stereoisomeric forms, namely, the *cis* and the *trans*. The existence of such pairs of isomerides is in complete harmony with the theoretical views of van't Hoff, and the only acid that exists in a larger number of isomeric forms than could be predicted from van't Hoff's views is cinnamic acid. The recent work of Biilmann (*Ber.*, 1909, 42, 182, 1443) indicates that certain of the isomerides of cinnamic acid are polymorphous forms (compare also Erlenmeyer, *ibid.*, 502, 513, 521; Liebermann, *ibid.*, 1027). According to Erlenmeyer (*Ber.*, 1905, 38, 3499; 1906, 39, 285, 1570), both *allocinnamic* acid and ordinary synthetical cinnamic acid yield two isomeric salts with brucine, and by this method a resolution of the two acids was accomplished.

The subsequent work of Marckwald and Meth (*Ber.*, 1906, 39, 2598) has shown that the two brucine salts derived from cinnamic acid are not isomeric, but that the salt melting at 135° is an acid salt, and the one melting at 113° a normal salt: Erlenmeyer's presumed resolution of synthetical cinnamic acid appears to be incorrect, and it is suggested by Marckwald that the same holds good for the resolution of *allocinnamic* acid.

We have made several experiments with alkaloidal salts of α -bromocinnamic and α -bromo*allocinnamic* acids with the object of seeing whether these acids can be resolved (compare Sudborough and Thompson, *Trans.*, 1903, 83, 1167). The strychnine salts proved to be the most suitable, as they crystallise well from alcohol. In the case of the α -bromo*allo*-acid we obtained two distinct crystalline salts, one melting at 183° (decomp.) and the other at 127° , but subsequent investigation proved that the second salt was merely the hydrated form of the first salt. Similar results were obtained in the case of strychnine α -bromocinnamate.

Strychnine α -Bromoallocinnamate, $C_{21}H_{22}O_2N_2, C_9H_7O_2Br$.—16.7 Grams of finely powdered strychnine (1 mol.) were added to a solution of 11.35 grams of pure α -bromo*allocinnamic* acid (1 mol.) in 500 c.c. of absolute alcohol, and the whole warmed gently until a clear solution was obtained.

After three days, clusters of slender, prismatic crystals had separated. The mother liquor (α) was removed, and the crystals washed with

absolute alcohol and dried. The weight of crystals was 17.2 grams, or a 62 per cent. yield. The salt was crystallised three times from absolute alcohol, but the melting point remained constant at 183° (decomp.):

0.3512 gave 0.1197 AgBr. Br = 14.50.

$C_{21}H_{22}O_2N_2, C_9H_7O_2Br$ requires Br = 14.26 per cent.

The salt did not lose in weight when heated at 127° for some time, and was thus free from water or alcohol of crystallisation.

The salt was optically active. 1.250 Grams, made up to 50 c.c. with absolute alcohol, gave $\alpha - 1.684^\circ$ at 18° in a 4-dcm. tube, whence $[\alpha]_D^{18} - 16.84^\circ$.

The mother liquor (α) from the above salt, on spontaneous evaporation, yielded large, transparent crystals. These were washed with alcohol and dried. The crystals melted at 127° to a clear liquid, but when the temperature was raised slightly, the molten mass solidified and melted again at 183° (decomp.):

1.9115, heated at 127° for ten minutes, lost 0.0660. $H_2O = 3.45$.

1.2196, ,, ,, 95° until constant, lost 0.0377. $H_2O = 3.09$.

0.3660 gave 0.1200 AgBr. Br = 13.93.

$C_{21}H_{22}O_2N_2, C_9H_7O_2Br, H_2O$ requires $H_2O = 3.11$; Br = 13.82 per cent.

0.4132, dissolved in alcohol, required 20.0 c.c. of 0.03616 *N*-baryta;

Theory 19.7. 0.4862 required 23.1 c.c.; Theory 23.2.

1.2500 grams, made up to 50 c.c. with absolute alcohol, gave $\alpha - 1.658^\circ$ in a 4-dcm. tube at 18°, whence $[\alpha]_D^{18} - 16.58^\circ (\pm 0.066^\circ)$.

The same crystals were obtained when the salt was recrystallised from 50 per cent. aqueous alcohol, or when a mixture of strychnine and α -bromo*allocinnamic* acid, or the anhydrous salt described above, was crystallised from 50 per cent. alcohol.

The salts are more soluble in mixtures of alcohol and water than in either of the pure liquids. The acid recovered from them melted at 120°, and was optically inactive.

Strychnine α -bromocinnamate. $C_{21}H_{22}O_2N_2, C_9H_7O_2Br$, was prepared by dissolving 4.54 grams of the acid and 6.68 grams of strychnine in 200 c.c. of absolute alcohol. After several hours, a quantity of colourless plates were deposited, which, when washed with alcohol and dried in the air, formed a fine white powder melting at 182°. Yield 6.45 grams.

The mother liquor gave a further yield of the same type of crystals, and ultimately about 1.5 grams of clear, hard, prismatic needles. These were stable when exposed to the air and melted at about 130°, but then resolidified and melted again at 182°. Further examination showed that they were a hydrated form of the salt, for they may be

obtained by recrystallising the anhydrous salt from 50 per cent. alcohol.

Anhydrous Salt.—0.2045 gave 0.0694 AgBr. Br = 14.44.

$C_{21}H_{22}O_2N_2, C_9H_7O_2Br$ requires Br = 14.26 per cent.

0.300, dissolved in alcohol, required 14.45 c.c. of 0.03664*N*-baryta ; Theory 14.6.

1.250 grams, made up to 50 c.c. with absolute alcohol, gave $\alpha + 0.47^\circ$ in a 4-dcm. tube at 22° , whence $[\alpha]_D^{22} + 4.7^\circ$.

Hydrated Salt.—0.5801 gave 0.1880 AgBr. Br = 13.79.

2.5672, heated at 130° for one hour, lost 0.0886. $H_2O = 3.45$.

2.0760 ,, ,, 108° ,, three hours, lost 0.0684. $H_2O = 3.29$.

$C_{21}H_{22}O_2N_2, C_9H_7O_2Br, H_2O$ requires Br = 13.82 ; $H_2O = 3.11$ per cent.

The difference in rotation between the strychnine salts of the two stereoisomeric α -bromocinnamic acids is remarkable ($[\alpha]_D + 4.7^\circ$ and -16.84° respectively).

B.—*Action of Alcoholic Potassium Hydroxide on d- and l- $\alpha\beta$ -Dibromo- β -phenylpropionic Acid.*

Sudborough and Thompson (*Trans.*, 1903, 83, 666) have determined the proportions of α -bromocinnamic and *allocinnamic* acids obtained by the action of alkalis on *dl*- $\alpha\beta$ -dibromo- β -phenylpropionic acid. We have examined the action of alcoholic potassium hydroxide on *d*- and *l*- $\alpha\beta$ -dibromo- β -phenylpropionic acids, and find that the ratio of the two unsaturated acids formed is much the same as when the ordinary inactive dibromo-acid is used, and that the acids thus obtained are optically inactive.

We used Hirsch's method (*Ber.*, 1894, 27, 883) for the preparation of the active $\alpha\beta$ -dibromo- β -phenylpropionic acids. The rotation of the pure acids is $\pm 64^\circ$. As it was not essential for our purpose to obtain the acids quite pure, we were content to use a *d*-acid with $[\alpha]_D + 29^\circ$, obtained by recrystallising the brucine salt twice from absolute alcohol, and then decomposing with dilute hydrochloric acid. The *l*-acid obtained by extracting the cinchonidine salt of the *dl*-acid several times with boiling benzene, and decomposing the residue with dilute hydrochloric acid, had $[\alpha]_D - 38^\circ$.

The acids were treated with two equivalents of alcoholic potassium hydroxide at 0° , and the products worked up in the manner described already (*Trans.*, 1903, 83, 674). The results are given in the following table.

$\alpha\beta$ -Dibromo- β -phenylpropionic acid. $[\alpha]_D$.	Weight taken in grams.	Weight of α -bromo-acid.	Weight of α -bromo- <i>allo</i> -acid.	Ratio
+29°	2.0	0.15	0.9	1 : 6
-38	2.0	0.16	0.86	1 : 5.5
-38	6.0	0.45	3.45	1 : 7.7

The ratio obtained by Sudborough and Thompson from *dl*- $\alpha\beta$ -dibromo- β -phenylpropionic acid under similar conditions was 1 : 7.8.

The rather low values of the ratio obtained when only a small quantity of the dibromo-acid was used is due to the solubility of the *allo*-acid in water.

C.—The Addition of Bromine to Esters of Cinnamic Acid.

By the addition of bromine to ethyl cinnamate under certain conditions, Michael (*Ber.*, 1901, 34, 3660) obtained as much as 54 per cent. of ethyl *allocinnamate* dibromide melting at 28—30°.

Sudborough and Thompson (*Trans.*, 1903, 83, 671) repeated some of Michael's experiments, but obtained as chief product the ordinary dibromide melting at 75—76°, only the merest traces of the *allo*-compound being formed.

Michael and Smith have recently performed a number of experiments on the bromination of the same ester (*Amer. Chem. J.*, 1908, 39, 27), using a slight excess of bromine, and working in carbon tetrachloride solution. In some of these experiments as much as 50 per cent. of the *allo*-dibromide was obtained, but they were unable to draw any general conclusions. They state that the yield of *allo*-compound depends on such subtle conditions that they do not consider the experiments as more than suggestive for future investigation. On the whole, the best yields were obtained when the solutions were not cooled, and where the bromine was added in portions. A comparison of their experiments also indicates that an increase in the length of time during which the mixture is kept tends to augment the yield of *allo*-compound.

We have made the following series of experiments :

Methyl Cinnamate and Bromine.—(1) 19.8 Grams of methyl cinnamate and 19.8 grams of dry bromine were dissolved separately in 100 c.c. of dry carbon disulphide. The bromine solution was added slowly in the dark at 0° to the ester solution, care being taken that the temperature did not rise. The mixture was then kept in an open vessel in the dark until all the solvent was removed, and the residual product was extracted several times with small amounts of cold carbon disulphide in order to extract the *allo*-dibromide. The yield of the latter was 5.6 per cent.

(2) Similar to 1. Yield, 5.25 per cent.

(3) Similar to 1, but only 50 c.c. of solvent were used, and the bromine solution was added quickly in diffused daylight. The temperature rose to 35°. Yield, 16.0 per cent.

(4) Similar to 3, but 100 c.c. of carbon disulphide were used, and

the temperature rose to the boiling point of the solvent. Yield, 12·7 per cent.

(5) Similar to 3, but the solvent was moistened by the addition of a drop of water. Yield, 12·2 per cent.

(6) Similar to 3, but the mixing was conducted in the evening, using artificial light. Yield, 8·75 per cent.

(7) Carbon tetrachloride was used as solvent; the bromine solution was added quickly at the ordinary temperature in diffused daylight. Yield, 16·5 per cent.

Ethyl Cinnamate and Bromine.—The ester used distilled at 260—264° under atmospheric pressure; in each experiment 20·7 grams of bromine were used for 22·0 grams of ester, each dissolved in 50 c.c. of solvent.

(1) Carbon disulphide was used as solvent, and the bromine solution was added rapidly in diffused daylight. The temperature rose to 43°. Slight evolution of hydrogen bromide took place, but no trace of the *allo*-dibromide could be isolated.

(2) Dry carbon tetrachloride was used as solvent, and the bromine solution was added in three portions at intervals of three hours. The admixture took place in the dark at 20—24°, and 7·0 per cent. of oily dibromide was obtained.

(3) Similar to 2, but the temperature was kept at 0°, and the addition occupied two days. Yield, 6·1 per cent.

(4) Similar to 2, but the two solutions were mixed at once, and the temperature was allowed to rise. Yield, 8·4 per cent.

Further experiments proved that methyl cinnamate dibromide (m. p. 118°) is not transformed into the *allo*-dibromide (m. p. 56°) when kept in contact with a solution of bromine in carbon disulphide or carbon tetrachloride for two months either in daylight or in the dark.

According to Erlenmeyer (*Ber.*, 1909, 42, 505), the ethyl ester of synthetical cinnamic acid is a mixture which can be partially resolved into its components by fractional distillation under diminished pressure. We intend to examine the products formed by the addition of bromine to the different fractions in order to determine whether it is the ester used which produces the discrepancies between Michael's results and our own.

D.—*The Action of Alkalis on the Dibromides of Methyl and Ethyl alloCinnamates.*

Previous experiments (*Trans.*, 1903, 83, 676) have shown that the chief product obtained by the elimination of hydrogen bromide from $\alpha\beta$ -dibromo- β -phenylpropionic acid is α -bromo*allo*cinnamic acid, the isomeric α -bromo-acid (m. p. 131°) being formed to a very slight

extent. When, however, esters are substituted for the acid dibromide, the chief product is the α -bromo-acid, and the yield of α -bromo*allo*-acid is considerably diminished. It is possible that the α -bromo*allo*-acid is to be regarded as the normal product in both cases, but that when esters are used the process of hydrolysis and elimination occur simultaneously and produce vibrations within the molecules which tend to cause the labile α -bromo*allo*-acid to pass over into the more stable α -bromo-acid.

The question as to the nature of the products formed by the elimination of hydrogen bromide from the *allo*-dibromides is of interest, and has received but little notice.

Michael (*Ber.*, 1901, 34, 3666) states that by boiling 3 grams of ethyl *allocinnamate* dibromide (m. p. 28°) with alcoholic sodium hydroxide solution he obtained 0.8 gram of α -bromo*allo*-acid (m. p. 120°) and 1.2 grams of α -bromo-acid (m. p. 131°).

We have made the following experiments :

(1) 5.6 Grams of methyl *allocinnamate* dibromide (m. p. 54—56°) were treated with two equivalents of potassium hydroxide in alcohol solution at 0°. The alcohol was subsequently removed by evaporation at the ordinary temperature, and the α -bromo-acids separated by means of their barium salts. 0.2 Gram of α -bromo*allo*-acid and 3.5 grams of α -bromo-acid were obtained. Theoretical yield, 3.95 grams.

(2) Six grams of ester (m. p. 54—56°) gave 3.8 grams of α -bromo-acid (m. p. 131°) and no trace of α -bromo*allo*-acid. Theoretical yield, 4.2 grams.

(3) Ethyl *allocinnamate* dibromide was purified by heating to 40° and filtering through glass wool with the aid of the pump. When cold it solidified to a crystalline mass, m. p. 30.1°.

2.17 Grams, with two equivalents of potassium hydroxide in alcoholic solution, gave 0.1 gram of α -bromo*allo*-acid and 1.05 grams of α -bromo-acid. Theoretical yield, 1.46 grams.

These results indicate that the main product of the reaction is the α -bromo-acid (m. p. 131°); in experiment (No. 2) no *allo*-acid could be isolated, and in the others the amount was very small, and may be due to admixture of the original *allo*-dibromide with small amounts of the isomeric dibromide, as it is extremely difficult to obtain these *allo*-dibromides in a pure state.

E.—Action of Organic Bases on $\alpha\beta$ -Dibromo- β -phenylpropionic Acid.

The only experiments conducted hitherto appear to be those of Sudborough and Thompson (*Trans.*, 1903, 83, 681), who obtained cinnamic acid and bromostyrene by boiling an alcoholic solution of dibromo- β -phenylpropionic acid with dimethylaniline.

We have repeated these experiments, and can confirm the results. From 10 grams of the dibromo-acid, 1.5 grams of cinnamic acid were obtained. After crystallisation from benzene, the acid melted at 133° ; it also crystallised from ether in aggregates of thin lamellæ resembling synthetical cinnamic acid. The recovered base contained small amounts of bromine.

Trimethylamine.—A solution of 6 grams of dibromo- β -phenylpropionic acid and 2.5 grams of trimethylamine in 25 c.c. of methyl alcohol was boiled for 0.5 hour in a reflux apparatus. The product was a mixture of 0.5 gram of α -bromocinnamic acid (m. p. 131°) and an oil, probably bromostyrene. Another experiment was made by keeping the alcoholic solution for forty days at the ordinary temperature and then removing the alcohol; an 80 per cent. yield of mixed α -bromo-acids was obtained. These were separated by means of their barium salts, when a 26.5 per cent. yield of α -bromo-acids (m. p. 131°) and a 47.7 per cent. yield of α -bromoallocinnamic acid (m. p., after recrystallisation, 120°) were obtained.

Diethylaniline.—When an alcoholic solution of $\alpha\beta$ -dibromo- β -phenylpropionic acid (10 grams) was boiled for an hour with diethylaniline (10 grams), 33 per cent. of the acid was recovered, and about 3 grams of an oil (bromostyrene) were formed.

Cinchonidine.—Eight grams of dibromo- β -phenylpropionic acid and 17 grams of cinchonidine were heated for a few minutes with 75 c.c. of absolute alcohol, and the clear solution kept for six weeks. 7.5 Grams of unaltered dibromo-acid were recovered. A second experiment was made by boiling the alcoholic solution of the dibromo-acid (10 grams) and cinchonidine (22 grams) for 1.5 hours. The product left after the removal of the alcohol was a gummy mass; this was treated with hydrochloric acid and shaken three times with ether. The ethereal solution was washed with a little water, and then extracted with dilute sodium carbonate solution. The aqueous alkaline solution was acidified with moderately concentrated hydrochloric acid, and gave 1.0 gram of organic acids, which were separated by means of their barium salts. The products obtained were bromostyrene, b. p. 215 — 220° , 4.7 grams = 79 per cent., α -bromocinnamic acid, 0.55 gram = 7.5 per cent., and α -bromoallocinnamic acid, 0.35 gram = 4.8 per cent. Total, 92.5 per cent.

Quinine.—Ten grams of the dibromo-acid gave 4.1 grams of bromostyrene and 0.6 gram of α -bromocinnamic acid.

Brucine.—Ten grams of dibromo- β -phenylpropionic acid, 26 grams of brucine, and 100 c.c. of absolute alcohol were heated for a few minutes and then evaporated to dryness on the water-bath, the whole operation taking some forty-five minutes. The products were bromo-

styrene, 40 per cent., α -bromo-acid, 21.7 per cent., and α -bromoallo-acid 24.4 per cent. Total, 86 per cent.

In all these experiments with feeble bases and alkaloids, appreciable amounts of bromostyrene are formed, but the most interesting result is that in practically every case the ratio α -bromo-acid/ α -bromoallo-acid is much greater than when strong alkalis are used. Thus with potassium hydroxide the ratio is one-seventh, whereas with trimethylamine it is, roughly, one half.

We wish to express our thanks to the Research Fund Committee for a grant which has covered part of the cost of this investigation.

THE EDWARD DAVIES CHEMICAL LABORATORIES,
UNIVERSITY COLLEGE OF WALES,
ABERYSTWYTH.

CLXXIV.—*The Constitution of Glucose Derivatives.*
Part II. Condensation Derivatives of Glucose with
Aromatic Amino-compounds.

By JAMES COLQUHOUN IRVINE and ROBERT GILMOUR, B.Sc.
(Carnegie Scholar).

THE mutarotation displayed by glucoseanilide and tetramethyl glucoseanilide has, in a previous communication (Trans., 1908, 93, 1429), been explained on the assumption that these compounds exist in stereoisomeric interconvertible forms which possess the γ -oxydic linking characteristic of reducing sugars and glucosides. From analogy it might be expected that the condensation compounds of glucose with amino-bases generally, and also with amino-acids, should be constituted in a similar fashion, and in the present paper we describe the results obtained in the examination of glucose-*p*-toluidide, -*p*-phenetidide, - β -naphthylamide, and -*o*-carboxyanilide. As Behrend and his pupils are at present engaged in similar work on the glucose-phenylhydrazones, we have not in the meantime extended our observations on these compounds.

The glucose derivatives mentioned above have now been shown to exist in interconvertible stereoisomeric forms which closely resemble the α - and β -glucoseanilides, and they may thus be similarly regarded as derivatives of the sugar in its γ -oxydic form. Compared with

what may be termed "normal glucosides,"* the compounds mentioned are peculiarly unstable, especially toward the action of hydrolytic agents, and it is thus impossible to apply chemical methods in elucidating their structure. Even the silver oxide reaction which has proved efficacious with other sugar derivatives, resulted in the present cases in molecular rupture, and thus evidence regarding constitution was sought for in the physical study of the formation and interconversion of the various isomeric forms of the compounds. We have prepared each of the above substances under conditions which permit of observation of the changes in rotatory power undergone during the condensations, and this has been supplemented by the detailed study of the mutarotation of the products. The claim for regarding the above compounds as γ -oxides thus rests on analogy alone, but their close similarity with the glucoseanilides, for which the γ -oxydic formula is supported by synthetical evidence (*loc. cit.*), leaves no reasonable doubt that all the substances are similarly constituted.

Glucose-p-toluidide.

This compound has already been prepared by Sorokin, who describes it as melting at 100° , and showing $a_D -43.8^{\circ}$ in methyl-alcoholic solution. On adopting his method of preparation, which consists in boiling an alcoholic solution of glucose with *p*-toluidine and precipitating the product with ether, we found that the success of the process depends largely on the amount of water which is present. Using anhydrous materials throughout, the product was a viscid syrup which did not solidify, but, on the other hand, the use of 83 per cent. alcohol as the solvent gave satisfactory yields of crystalline material. The amount of the solvent alcohol and the quality of the ether used as the precipitant are, however, important points. Pure dry ether gives a product crystallising in square plates, whilst ordinary commercial ether precipitates the compound in well-formed needles, apparently identical with the form described by Sorokin. A third form, crystallising in prisms, was obtained by boiling either of the above varieties with a large excess of ethyl acetate. Although the toluidide is only sparingly soluble in this solvent, the crystalline form of the undissolved residue continually altered during this treatment, indicating that the process involved simultaneous solution and crystallisation. The detailed examination of this third variety showed that it is the anhydrous form.

Examination of Glucose-p-toluidide Crystallising in Needles.—The details of the preparation of this compound are as follows: Sixty grams

* That is, compounds in which the sugar residue is linked to the remaining group through oxygen.

of powdered glucose were added to a solution of 120 grams of *p*-toluidine in one litre of 83 per cent. alcohol, and dissolved at the boiling point. After boiling for one hour, the solution was evaporated until 800 c.c. of alcohol had been collected, and the residual syrup was then mixed with four times its volume of ether. The oil solidified almost immediately to a mass of delicate needles, which were collected, washed with ether, and dried in a vacuum desiccator. The substance decomposed readily on heating, and the melting point, although considerably higher than that quoted by Sorokin, was indefinite (115—120°). Analysis of the air-dried material indicated the presence of one molecule of water of crystallisation:

Found: C = 54.26; H = 7.37.

$C_{13}H_{19}O_5N, H_2O$ requires C = 54.35; H = 7.31 per cent.

In all the preparations the products were lævorotatory, and showed downward mutarotation. When precipitated by ether as described above, the first crops obtained were invariably more highly active than succeeding crops, but the equilibrium values attained in solution were fairly uniform. In determining the mutarotation, methyl alcohol was used as the solvent, and the concentration was, as nearly as possible, 2.500 in each case.

	Initial $[\alpha]_D$.		Permanent $[\alpha]_D$.
Crop 1	- 97.6°	—————>	- 45.2°
„ 2	- 87.5	—————>	- 44.9
„ 3	- 21.8	—————>	- 45.0

We regard this lævorotatory variety as the hydrated β -form.

Examination of Glucose-p-toluidide Crystallising in Plates.—This variety of the toluidide may be prepared by Sorokin's process, the amount of 83 per cent. alcohol employed as a solvent being not more than twelve times the weight of sugar used. With these proportions, dry ether must be used in the precipitation of the product. The pure compound, when recrystallised from anhydrous methyl alcohol, melted without appreciable decomposition at 117—119°, and analysis showed that half a molecule of water of crystallisation was present:

Found: C = 56.00; H = 7.35.

$C_{13}H_{19}O_5N, \frac{1}{2}H_2O$ requires C = 56.11; H = 7.19 per cent.

The first crops of the compound to be precipitated contained excess of the lævo-form, whilst succeeding crops contained a larger proportion of the dextro-isomeride than exists in the equilibrium mixture; mutarotation in opposite directions was thus observed.

	Initial $[\alpha]_D^{20^\circ}$.		Final $[\alpha]_D^{20^\circ}$.		Initial $[\alpha]_D^{20^\circ}$.
Crop 1.....	- 94.6°	—————>	- 47.3°		—
„ 2.....	—		- 45.0	—————<	- 21.1°

The compound combined readily with an additional half-molecule of water to give the monoclinic variety, the change being effected by crystallisation either from water or from dilute methyl alcohol. The fact that during this treatment the compound gained about 3 per cent. of its weight is also consistent with the idea that the change is due to the addition of water. This transformation from the plate form to the needle variety has little effect on the rotatory power of the compound. This is seen whether we compare the initial values or the permanent specific rotations attained in solution :

	Initial $[\alpha]_D^{20}$.		Final $[\alpha]_D^{20}$.
Needle form	- 97·6°	—————>	- 45·2°
Plate ,,	- 94·6	—————>	- 47·3°

These slight differences in rotatory power are somewhat greater than the experimental error of our observations, but it is noteworthy that the permanent values become identical if the concentrations be calculated in each case for the amount of the anhydrous compound present in the solution.

As the initial specific rotation quoted above (- 94·6°) was obtained with a specimen which had been repeatedly crystallised from absolute methyl alcohol, it probably approximates closely to the maximum value for the partly hydrated β -toluidide.

Examination of Glucose-p-toluidide Crystallising in Prisms.—In our experience the most convenient method of preparing anhydrous glucose-p-toluidide is to use anhydrous materials in Sorokin's process. The product thus obtained was a syrup, which became crystalline when boiled for about one hour with a large excess of ethyl acetate. The residue then crystallised from methyl alcohol in long, slender prisms, which analysis showed to be the anhydrous compound :

Found : C = 57·55 ; H = 7·15.

$C_{13}H_{19}O_5N$ requires C = 57·99 ; H = 7·06 per cent.

The compound may be converted into the hydrated varieties already described by solution in dilute alcohol and removal of the solvent. In this way a mixture of plates and needles was obtained, and on repeating the process the needle form alone was finally produced. Conversely, prolonged boiling of either of the hydrated forms with ethyl acetate resulted in almost complete conversion into the anhydrous compound. A 2 per cent. solution of the prismatic toluidide in methyl alcohol was strongly dextrorotatory, the maximum value observed being $[\alpha]_D^{20}$ 181·9°. The mutarotation was extremely rapid, particularly in presence of traces of acid, the average end point being $[\alpha]_D$ - 45°. It was found possible to obtain a specimen of the compound containing a greater proportion of the lævo-form than exists in the equilibrium mixture by evaporating the alcohol from a solution which had

attained the permanent rotatory power, and boiling the crystalline residue with ethyl acetate. After boiling for one hour, the liquid was filtered. The undissolved residue now gave α_D 163° , whilst the filtrate yielded a crop showing $[\alpha]_D - 69^\circ$. The two specimens were identical in analytical composition, showed mutarotation in opposite directions, and gave the same equilibrium value in solution. The boiling with ethyl acetate evidently effected a transformation of the lævo- into the dextro-isomeride, and did not consist merely in the extraction of one form by the solvent. This was shown by the fact that on prolonged boiling the amount of the lævo-form present in the solution diminished, until ultimately practically the whole of the material was deposited in the form of the sparingly soluble dextro-variety.

The results of the above experiments therefore show that, when prepared by the ordinary method, anhydrous glucose-*p*-toluidide contains excess of the dextrorotatory α -form; on the other hand, the β -isomeride is lævorotatory, and shows a ready tendency to crystallise with water of crystallisation.

Optical Effect of Condensing Glucose with p-Toluidine.—The polarimetric study of the condensation of glucose with *p*-toluidine afforded evidence as to the mechanism of the reaction. Five grams of glucose were dissolved in 50 c.c. of 83 per cent. alcohol, and the solution kept for several days. Excess of *p*-toluidine (8 grams) was then added, and the liquid kept at 14° , daily observations of the rotation being made:

Time in days.	α_D (2-dcm. tube).	Time in days.	α_D (2-dcm. tube).
0	+7.05°	3	+1.40°
1	7.70	7	-7.75
2	5.00	10	-10.25

The well-marked increase and diminution in the dextro-sense would correspond with the formation in the first instance of the anhydrous prismatic α -form, which would undergo reversible change to give the equilibrium mixture of the α - and β -modifications. The latter form is then, according to the amount of water present, partly or completely hydrated, giving rise ultimately to the needle variety.

Effect of Boiling Glucose-p-toluidide with Ether.—In the case of the glucoseanilides it was found possible to effect a partial separation of the α - and β -forms by extraction with a large excess of boiling ether. On applying the same process to the β -form of glucose-*p*-toluidide a different result was, however, obtained. Even after prolonged boiling, the ethereal filtrate was found to be quite inactive, and the extract then contained only a small quantity of oil in solution. The rotation of the undissolved residue nevertheless altered continuously during the treatment, at first increasing in the lævo-sense and afterwards dimin-

ishing, until ultimately the substance showed a distinct dextrorotation. This change was not, however, due to interconversion of the α - and β -forms, but is attributable to extremely slow hydrolysis. This was shown by the fact that the equilibrium values attained in solution by specimens of the compound treated in this way also altered during the process, showing a continuous fall in the lævo-sense:

Time in hours.	Initial α_D .		Final α_D .	Time in hours.	Initial α_D .		Final α_D .
0	-48.2°	→	-40.7°	4	-85.9°	→	-28.9°
1	99.2	→	37.0	7	-67.0	→	-22.0
2	97.4	→	36.0	100	+4.9	→	+5.8

It was also found that the nitrogen content diminished steadily throughout the treatment with ether, and the above results are explained on the assumption that slow hydrolysis took place. The rate of this hydrolysis naturally varied with the quantity and quality of the ether used. With carefully purified ether, however, no alteration in the optical values of the toluide were observed when special precautions were taken to exclude moisture during the heating. The result is interesting as indicating the extreme sensibility of these compounds towards hydrolytic agents.

Glucose-p-phenetidide.

Our experience with this compound is somewhat at variance* with that recorded by Claus and Rée (*Chem. Centr.*, 1898, ii, 695), who state that the substance crystallises, presumably in the anhydrous form, in needles melting at 160°. No previous examination of the rotatory powers of the compound seems to have been made. The method of preparation followed by us in the first instance was exactly the same as for glucose-*p*-toluidide. The crystalline product thus obtained softened at 95° and melted completely, and decomposed between 110° and 120°. Considerable difficulty was experienced in obtaining satisfactory analytical figures for the phenetidide when prepared either by the method mentioned above or by the process of slow condensation which is subsequently described. When the crystalline substance was dried in air, the figures obtained corresponded with the presence of one molecule of water of crystallisation:

Found: C = 52.40; H = 7.30; OEt = 14.58.

$C_{14}H_{21}O_6N, H_2O$ requires C = 52.99; H = 7.26; OEt = 14.19 per cent.

The substance lost in weight when preserved in a vacuum desiccator,

* Other observers have had occasion to question the reliability of previous work on this compound. In a recent paper, St. Mostowski (*Bull. Acad. Sci. Cracov*, 1909, 641) contradicts the generally accepted statement that glucosphenetidide possesses powerful toxic properties.

and analyses of specimens dried in this way gave figures varying between values calculated for the hydrated and anhydrous forms. On heating for several hours at 60° in a vacuum, the loss in weight corresponded with the removal of half a molecule of water, and the residue on combustion gave figures agreeing approximately with this supposition :

Found : C = 53.92 ; H = 7.14.

$C_{14}H_{21}O_6N, \frac{1}{2}H_2O$ requires C = 54.54 ; H = 7.14 per cent.

All attempts to obtain the completely dehydrated form failed, although the method of preparation was modified in various ways. Considering the discrepancy between our results and those quoted in the literature, we redetermined the molecular weight in ethyl-alcoholic solution by the ebullioscopic method and obtained a normal result :

Found : M.W. = 312 ; $C_{14}H_{21}O_6N, H_2O$ requires M.W. = 317.

In every other respect our preparation resembled that described by Claus and Réé.

The specific rotation of the hydrated compound in methyl-alcoholic solution ($c = 3.4660$) was -96.1° , but this rapidly altered to the constant value, -38.3° . On account of the low melting point of the compound, the usual method of increasing the proportion of the lævo-form by boiling with ethyl acetate could not be applied, as the phenetide fused under the liquid and the equilibrium mixture of the two forms was thus obtained. It was also found that when boiled with specially purified ether no transformation of the mutarotatory forms took place, although the use of commercial ether, probably on account of hydrolytic action, considerably increased the lævorotation of the undissolved residue.

The mutarotation mentioned above indicates the existence of a dextrorotatory variety of the phenetide, and this was confirmed by observing the optical changes which took place during the condensation of the sugar with the base. A 3 per cent. solution of glucose was prepared in 83 per cent. alcohol, and 6 grams of *p*-phenetidine were dissolved in 100 c.c. of the solution. On keeping the liquid at 14°, it was found that the rotation decreased continuously ; after six days the solution was lævorotatory, and on the eleventh day the product commenced to crystallise in beautiful long needles. With higher concentrations the condensation proceeded much more rapidly, and with a 9 per cent. solution of the sugar the change was complete in about eight hours. The following table contains the rotations then observed in a 2-dcm. tube :

Time in minutes.	α_D .	Time in minutes.	α_D .
0	+6.16°	120	+3.94°
30	5.90	240	+1.20
60	5.40	480	-3.00

The slow initial decrease in the first stages of the reaction is evidently followed by a more rapid diminution. The total optical effect is due to: (1) formation in unequal amounts of the α - and β -forms of the phenetidine, (2) mutarotation of the uncombined sugar, (3) mutarotation of the phenetidine formed. Taking these factors into account, the readiest explanation of the above polarimetric results is that the form of the phenetidine first produced has a dextrorotation higher than that of glucose, and the reaction is thus brought into line with the condensation of the sugar with *p*-toluidine and with β -naphthylamine.

Glucose- β -naphthylamide.

The usual method of condensing glucose with amino-compounds proved efficacious in the preparation of glucose- β -naphthylamide. A solution of 20 grams of β -naphthylamine in 300 c.c. of alcohol (83 per cent.) was boiled under a condenser with 10 grams of glucose. After one hour's treatment, the sugar had completely dissolved. Most of the solvent was then removed, and a large excess of ether added to the solution. A copious precipitate of delicate needles, closely resembling glucose-*p*-phenetidine, was at once deposited. The product, after collection and washing with dry ether, melted sharply at 117°. Analysis of the air-dried specimen gave:

Found: C = 59.20; H = 6.80:

$C_{16}H_{19}O_5N, H_2O$ requires C = 59.44; H = 6.50 per cent.

In different preparations the rotatory power of the compound was fairly uniform, the initial value found for a 2.5 per cent. solution in methyl alcohol varying between $[\alpha]_D^{20} - 111^\circ$ and $[\alpha]_D^{20} - 97^\circ$. Mutarotation invariably occurred with these solutions, the constant value $[\alpha]_D^{20} - 48.1^\circ$ being reached in each case. The compound therefore exists in two stereoisomeric forms, one of which (the β -form) is strongly lævo- and the other (the α -form) probably dextro-rotatory.

On boiling a specimen of the compound for five hours with a large excess of ether, the specific rotation of the undissolved residue increased from -96.7° to -118.7° . This behaviour is similar to that observed with glucosetoluidide, and is no doubt attributable to the same causes. As in this case the undissolved residue would contain free glucose, the value mentioned above must be taken merely as an indication of the fact that β -glucose- β -naphthylamide possesses a very high lævo-rotation.

Evidence that, in addition to the β -isomeride, a dextrorotatory α -form exists was obtained in the polarimetric study of the formation of the compound. A 3 per cent. solution of glucose in 83 per cent. alcohol was prepared and allowed to attain the constant rotatory power. Six grams of β -naphthylamine were then dissolved in 100 c.c.

of this solution, the liquid being afterwards maintained at 15° for several days. The dextrorotation at first increased rapidly and then regularly diminished, the solution ultimately becoming levorotatory.

Time in hours.	α_D (2-dex. tube).	Time in hours.	α_D (2-dem. tube).
0	+2.94°	9	+2.45°
3	3.00	24	+1.05
6	2.78	100	-1.50

The rotation solution subsequently deposited the compound in well-formed needles more than half an inch in length. Analysis showed that in this case, also, the compound contains one molecule of water of crystallisation. Other hydrated forms of the compound doubtless exist, as when crystallised from ethyl acetate a mixture of needles and plates was obtained. The latter variety could not be obtained unmixed with the needle form, but from the analogy of glucose-*p*-toluidide it probably contains half a molecule of water of crystallisation. It will thus be seen that in every respect glucosenaphthylamide is closely analogous to the corresponding toluidide.

An attempt to condense glucose with α -naphthylamine led to no definite result. The unaltered sugar was recovered in the crystalline state and no condensation products could be detected.

Glucose-o-carboxyanilide.

It is already known that glucose condenses with 2:3-diaminobenzoic acid, but does not react with other isomeric forms of the compound. The constitution of the product has given rise to considerable discussion, and it is still doubtful if both of the amino-groups take part in the reaction. There seems every reason to believe, however, that the carboxyl group remains intact in the process. The problem is naturally simplified by the substitution of a monoamino-acid for the diamino-compound, and in the hope of obtaining some information regarding the mechanism of the condensation of sugars with amino-acids generally, we have prepared and examined glucose-*o*-carboxyanilide.

On boiling an alcoholic solution of glucose with anthranilic acid, extensive decomposition takes place, and very little product is obtained. At the ordinary temperature, however, the condensation proceeds smoothly, and the change may thus be followed polarimetrically. The results obtained in the following typical preparation show that at 18° the change is rapid, and although the activity decreases continuously, the diminution is comparatively slow in the early stages of the reaction, thus indicating that the form first produced is more strongly dextrorotatory than glucose. A 9 per cent. solution of glucose was kept until constant in rotation. Twenty grams

of anthranilic acid were then dissolved in 150 c.c. of the solution, which was at once placed in a thermostat at 18°, a polarimetric sample being meanwhile kept at the same temperature in a 2-dcm. jacketed tube.

The following optical changes were then observed :

Time in minutes.	α_D .	Time in minutes.	α_D .
0	+8.25°	60	+7.50°
10	8.25	90	6.75
20	8.15	130	6.25
30	7.90		

After twenty hours the solution was levorotatory, and subsequently crystallisation of the product commenced. The compound separated in long needles, which, after washing with dry ether, melted at 128—130°. Analysis of the air-dried product showed that one molecule of water of crystallisation was present :

Found : C = 49.24 ; H = 5.95.

$C_{13}H_{17}O_7N, H_2O$ requires C = 49.21 ; H = 5.99 per cent.

A determination of the amount of combined water in the compound was necessary, as the analytical figures quoted above do not exclude the possibility of condensation of the sugar with the acid through both the amino- and carboxy-groups, giving a product crystallising with two molecules of water. On account of the instability of the compound, this determination had to be conducted at 80° in a vacuum. The substance then lost 3.1 per cent. of its weight, the calculated result for one molecule of water being 2.9 per cent.

Glucose-o-carboxyanilide is sparingly soluble in water, readily so in alcohol, and dissolves easily in sodium carbonate solution. The aqueous solution reacts feebly acid towards litmus, and, owing to molecular rupture, reduces Fehling's solution at the boiling point. The formation of the compound evidently consists in condensation of the constituents through the amino-group only, and the carboxy-group remains intact. This was shown by the formation of a definite sodium salt. On adding two molecular proportions of sodium ethoxide to a 3 per cent. solution of the compound in absolute ethyl alcohol, an abundant amorphous precipitate separated, which was rapidly collected and washed with alcohol. The salt, which was highly deliquescent, was dried until constant in weight in a vacuum desiccator :

Found : Na = 7.11.

$C_{13}H_{16}O_7NNa$ requires Na = 7.16 per cent.

The acid from which the sodium salt was derived must therefore possess the structure $C_6H_{11}O_5 \cdot NH \cdot C_6H_4 \cdot CO_2H$.

This formation of a mono-sodium derivative from glucose-*o*-carboxy-

anilide not only confirms the presence of the carboxy-group, but has some bearing on the constitution of the sodium glucosate. It is evident that in the latter compound the metallic atom must occupy the glucosidic position, as this is the only part of the sugar molecule which is substituted in glucose-*o*-carboxyanilide. Any alternative structure for sodium glucosate, other than that suggested, would involve the formation of a disodium compound under the conditions of the above experiment.

The optical study of glucose-*o*-carboxyanilide gave results closely analogous to those obtained with the other compounds described in this paper. All the preparations of the substance were dextro-rotatory, and displayed extremely rapid mutarotation in the laevo-direction, the permanent values being rather irregular, doubtless on account of slight hydrolysis. The effect of boiling with ethyl acetate was to increase the proportion of the dextrorotatory form, and it was shown by analysis that this change was entirely due to stereochemical alteration and not to partial dehydration of the hydrated compound. The following typical example of these optical changes may be given :

Solvent = methyl alcohol, $c = 2.500$, $t = 20^\circ$.

Initial specific rotation : $[\alpha]_D^{20} + 35.1^\circ$; permanent value, $+11.1^\circ$.

After boiling for three hours with excess of ethyl acetate the same specimen gave :

Initial specific rotation, $+87.4^\circ$; permanent value, $+14.5^\circ$.

The dextro-variety is therefore the form first produced, and is the less soluble form. We propose the name α -glucose-*o*-carboxyanilide for this dextro-form, and we consider that the interconversion of the two isomerides is consistent with the idea that they contain the γ -oxydic linking.

The expenses of the above research were defrayed by a special grant from the Carnegie Trust, for which the authors desire to express their thanks.

CHEMICAL RESEARCH LABORATORY,
UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD,
UNIVERSITY OF ST. ANDREWS.

CLXXV.—*The Relation between Viscosity and Chemical Constitution. Part IV. Viscosity and Hydration in Solution.*

By ALBERT ERNEST DUNSTAN and FERDINAND BERNARD THOLE.

THE problem of the existence or the non-existence of complexes in solution has in recent years been raised from the sphere of controversy into the region of experimental verity. In a monograph published by Washburn (*Tech. Quart.*, 1908, 21, 360 *et seq.*) a critical summary is given of the diverse methods on which so many chemists have based the conclusion, that not only may a compound have a continued existence as such in a solution, but also it may, in accordance with the laws of combination, form a more or less stable aggregate, which will, in general, exist in equilibrium with the solvent and the simple compound. During several years one of the present authors has been collecting data on the viscosity of solutions, and has at various times brought forward instances where viscosity-concentration curves attain a maximum, and it has been found invariably to be the case that such maxima occur at or near points of simple molecular composition. Moreover, viscosity in general increases with molecular weight, and liquids of known associative power have usually a considerably higher viscosity than those of a simpler type. The conclusion that such maxima indicate the existence of aggregates in the solution is thus a natural one, and has been supported in recent years by the work of Getman (*J. Chim. phys.*, 1906, 4, 386), Kremann and Ehrlich (*Sitzungsber. Wien. Akad.*, 1907, 116, 740), Beck and Ebbinghaus (*Zeitsch. physikal. Chem.*, 1907, 58, 436), and Tsakalotos (*Bull. Soc. chim.*, 1908, [iv], 3, 224, 242). Some objections have been raised, however, against this view. Senter (*Physical Chemistry*, 1908, p. 306) draws attention to the statement of Arrhenius that non-electrolytes in general raise the viscosity of water, and hence a maximum point is almost certain to be attained on the viscosity-concentration curve. But it is precisely because combination or association goes on that the viscosity rises even when the viscosity of the added component is less than that of water. The maximum point is reached when the proportions of the liquids are in the most favourable ratio demanded by the laws of combination and of mass action. Washburn (*loc. cit.*), in connexion with such changes of curvature, states "although the existence of points of discontinuity can be denied, yet striking irregularities sometimes occur," and further, quotes the work of Küster and Kremann (*Zeitsch. anorg. Chem.*, 1904, 41, 31), who found

very distinctly marked discontinuities in the curves connecting the expansion coefficients with concentrations for aqueous solutions of nitric acid. These irregularities occurred at the concentrations required for the existence of $\text{HNO}_3, \text{H}_2\text{O}$ and $\text{HNO}_3, 3\text{H}_2\text{O}$. Precisely similar results were obtained by Kremann and Ehrlich (*loc. cit.*, 749), who determined the existence of the complex $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$, a hydrate, the reality of which has been indicated by almost every variety of physico-chemical method (Dunstan and Wilson, *Trans.*, 1907, 91, 83). Thus there can be little doubt as to the physical meaning of the maximum points on such property-concentration curves. As to the occurrence of minor changes of curvature, they may be denied altogether (Washburn, p. 409), although this involves the denial of the irreproachable accuracy of Pickering's work; they may be set down to erroneous methods of plotting (Hartley, Thomas, and Applebey, *Trans.*, 1908, 93, 541), or, finally, they may have a real existence.

Much of the present conflicting data must be revised before a final answer can be given. In the present communication the authors have endeavoured to collect further evidence bearing on the actual existence of genuine complexes in solution. To this end four pairs of liquids have been examined, and these four pairs have been chosen because so much work has been carried out with them at various temperatures by a considerable number of investigators, for example, Poisseule (*Mem. Instit. Paris*, 1846, 9, 433), Graham (*Phil. Trans.*, 1861, 151, 373), Wijkander (*Wied. Beibl.*, 1879, 8, 3), Noack (*Ann. Phys. Chem.*, 1886, [iii], 27, 289), Traube (*Ber.*, 1886, 19, 871), Arrhenius (*Zeitsch. physikal. Chem.*, 1887, 1, 285), Varenne and Godefroy (*Compt. rend.*, 1903, 137, 993), Dunstan (*Trans.*, 1904, 85, 817; 1905, 87, 11), and Getman (*loc. cit.*). With the exception of very slight details, the curves obtained by the above chemists are identical, and the general agreement that these liquid mixtures afford well defined maxima is irreproachable.

The viscosity-concentration curves for these pairs of liquids have been determined at 20°, 25°, and 30°, and the chief object has been to settle whether any appreciable shift of maximum takes place with varying temperature. Some difference of opinion seems to exist on this point. Senter (*loc. cit.*) draws attention to this possible variation of the position of the maximum point, and considers that any alteration therein invalidates the conception of definite hydrates in solution. It appears to the present authors that the lability of a complex in solution is so great that any alteration in temperature or in concentration may alter the equilibrium to a more or less pronounced extent. For example :

Arrhenius found that the maximum point in the system
 $C_2H_5 \cdot OH - H_2O$
 changed as follows:

Maximum at per cent. alcohol.		Temperature.	Traube: $C_2H_5 \cdot OH - H_2O$.	
			Maximum for ethyl alcohol.	Temperature.
36		0°	36	0°
42		17	41	10
50		55	46	20
Traube: $CH_3 \cdot OH - H_2O$.			46	30
Maximum at per cent. methyl alcohol.			$C_3H_7 \cdot OH - H_2O$.	
			Maximum for <i>n</i> -propyl alcohol.	
32		0°	48	0°
34		10	50	10
37		20	54	20
40		30		

Getman for the system methyl alcohol-water found the maximum point practically unchanged for a range 0—63°, and so, also, Wijkander observed in the case of the system acetic acid-water. Domke and Bein for the system sulphuric acid-water noticed that the discontinuities already referred to were invariant with regard to temperature changes, and Kremann and Ehrlich showed that the viscosity maximum at H_2SO_4, H_2O did not change within the limits 0—75°; this same maximum was further demonstrated by Domke and Bein, Knietsch (*Ber.*, 1901, **34**, 4069), and Dunstan and Wilson. Moreover, Kremann and Ehrlich noted that the maximum points in the systems aniline-phenol and aniline-cresol were invariant through a temperature range of 88°. The results brought forward in the present communication show that the variation of the maximum point in the four cases specified is so small as to be almost negligible. It is certainly difficult to demonstrate any appreciable change on a curve. The conclusion seems to be that, not only do these aggregates exist in solution, but also they have a certain temperature range of stability, which is greater for aqueous solutions of acids than for similar solutions of alcohols.

EXPERIMENTAL.

The method and apparatus have been described previously (*Trans.*, 1904, **85**, 817; 1905, **87**, 11; 1907, **91**, 1730). New stop-watches supplied and kept in order by Messrs. Dent have been used, and temperature variations have been kept within 0.01° by means of a large thermoregulator checked by a Beckmann thermometer. Following a suggestion by Hartley, conductivity water has been employed both as a solvent and for rinsing the viscometers. The materials were Kahlbaum's purest preparations. Appropriate dehydration and fractionation were employed.

Methyl Alcohol (b. p. 65.4°/765 mm.) and *Water*.

Per cent. CH ₃ ·OH.	20°.		25°.		30°.	
	Sp. gr.	η .	Sp. gr.	η .	Sp. gr.	η .
100.00	0.7923	0.005852	0.7878	0.005525	0.7835	0.005151
79.64	0.8481	0.01115	0.8135	0.01003	0.8391	0.009098
58.61	0.8977	0.01593	0.8940	0.01399	0.8901	0.01249
37.82	0.9384	0.01816	0.9355	0.01567	0.9325	0.01379
19.74	0.9671	0.01587	0.9650	0.01378	0.9628	0.01198
0.00	0.9983	0.01002	0.9972	0.00891	0.9958	0.00798

Ethyl Alcohol (b. p. 79.2°/772 mm.) and *Water*.

Per cent. C ₂ H ₅ ·OH.	20°.		25°.		30°.	
	Sp. gr.	η .	Sp. gr.	η .	Sp. gr.	η .
99.20	0.7922	0.01241	0.7876	0.01115	0.7832	0.009905
78.09	0.8481	0.02004	0.8439	0.01804	0.8399	0.01530
61.85	0.8871	0.02510	0.8828	0.02173	0.8786	0.01834
45.57	0.9237	0.02797	0.9266	0.02351	0.9165	0.01987
39.65	0.9359	0.02789	0.9323	0.02343	0.9293	0.01936
20.71	0.9677	0.02162	0.9654	0.01829	0.9629	0.01505
0.00	0.9983	0.01002	0.9972	0.00891	0.9958	0.00798

n-Propyl Alcohol (b. p. 97.7°/759 mm.) and *Water*.

Per cent. C ₃ H ₇ ·OH.	20°.		25°.		30°.	
	Sp. gr.	η .	Sp. gr.	η .	Sp. gr.	η .
100.00	0.8057	0.02180	0.8011	0.01936	0.7970	0.01736
73.13	0.8623	0.02938	0.8584	0.02509	0.8543	0.02169
59.38	0.8918	0.03148	0.8867	0.02652	0.8831	0.02306
28.62	0.9536	0.02548	0.9494	0.02118	0.9476	0.01812
17.40	0.9746	0.02010	0.9723	0.01697	0.9699	0.01440
0.00	0.9983	0.01002	0.9972	0.00891	0.9958	0.00798

Acetic Acid (b. p. 118—118.5°/759 mm.) and *Water*.

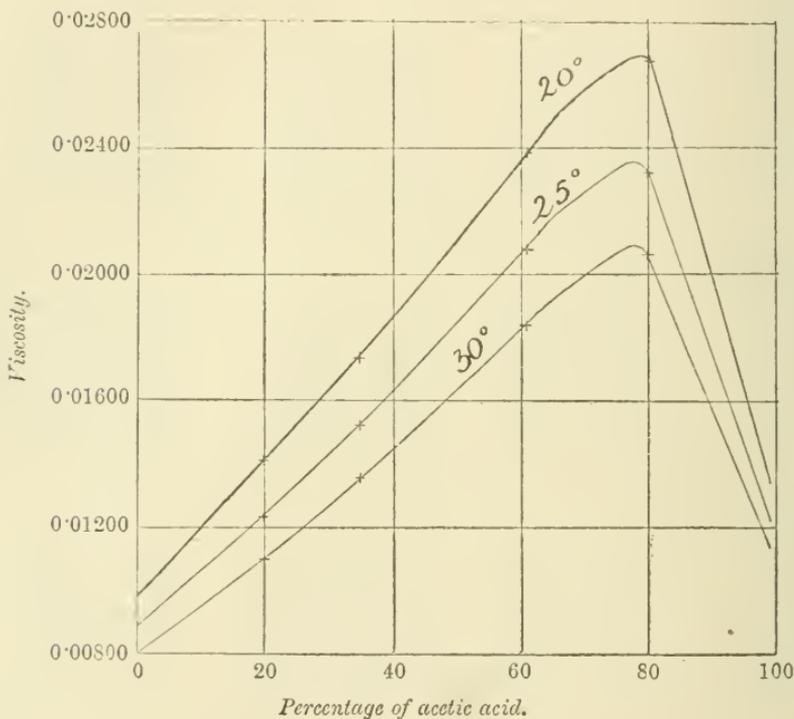
Per cent. C ₂ H ₄ O ₂ .	20°.		25°.		30°.	
	Sp. gr.	η .	Sp. gr.	η .	Sp. gr.	η .
99.15	1.0522	0.01333	1.0466	0.01223	1.0407	0.01140
80.00	1.0699	0.02675	1.0647	0.02319	1.0596	0.02064
60.80	1.0648	0.02392	1.0602	0.02077	1.0557	0.01842
35.17	1.0433	0.01742	1.0401	0.01529	1.0377	0.01361
19.88	1.0260	0.01407	1.0233	0.01234	1.0209	0.01099
0.00	0.9983	0.01002	0.9972	0.00891	0.9958	0.00798

An examination of the viscosity-concentration curves (Figs. 1 and 2) shows that in each case* the set of three curves affords the same maximum point in agreement with Getman. The slight differences between these results and those of Traube at the same range of temperature amount only to 2.7 per cent. for methyl alcohol, 3.3 per cent. for ethyl alcohol, and 3 per cent. for *n*-propyl alcohol. It is evident that these small amounts might easily be caused by errors in plotting the curves. Further, it should be noticed that the curves flatten considerably as the temperature rises, the equilibrium alcohol α H₂O \rightleftharpoons

* The curves for methyl and *n*-propyl alcohols are precisely similar in character to that for ethyl alcohol, and are therefore not reproduced.

alcohol + $x\text{H}_2\text{O}$ tends to the vanishing point; indeed, Getman found that at 65° the methyl alcohol-water curve was not far removed from a straight line. This most important observation brings out still more forcibly the authors' contention that an explanation of maximum points is to be sought for in complex formation, for obviously at sufficiently high temperatures such association would be largely inhibited. A consideration of the curves shows that the viscosity temperature-coefficient for the pure components is relatively small, but that it progressively increases up to the maximum point. Now

FIG. 1.



this quantity, $d\eta/d\theta$, gives a further indication of the validity of the authors' contention. In the case of all associated liquids, $d\eta/d\theta$ is much greater than for unimolecular compounds.

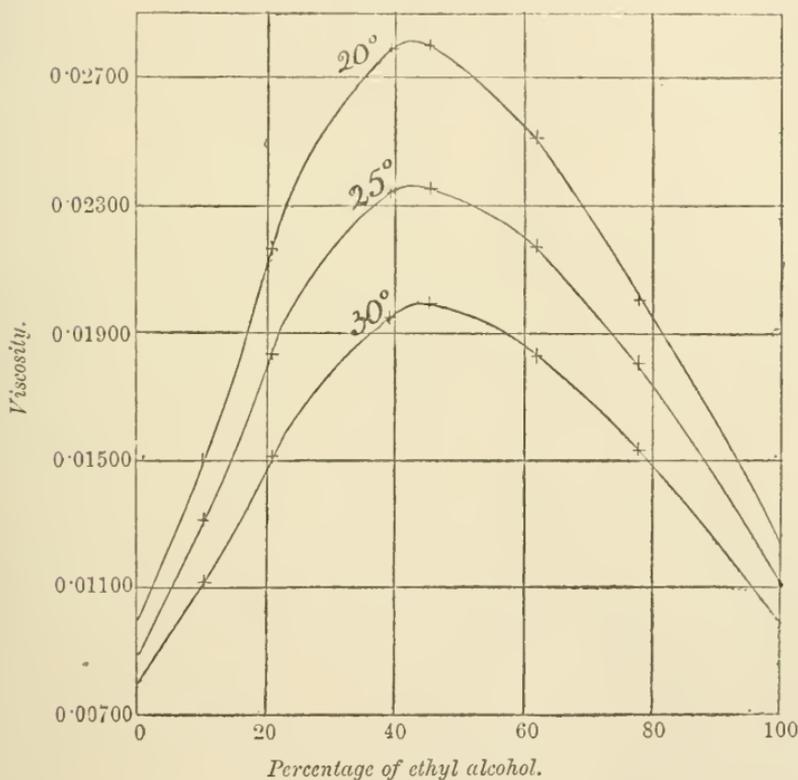
Liquid.	$d\eta/d\theta$ for $10-0^\circ$.
Methyl alcohol.....	0.00127
Ethyl ,,	0.00321
n-Propyl ,,	0.00965
Propionic acid	0.00333
Methyl formate	0.00045
Ethyl ,,	0.00057
Propyl chloride	0.00056
Methyl iodide	0.00058

Thus the value of the temperature-coefficient is a certain test for association.

Consider now the values for $d\eta/d\theta$ in the cases of the four pairs of liquids chosen.

Liquid pair.	Value of $d\eta/d\theta$ at 20—30°.
$H_2O-CH_3\cdot CO_2H$	0·006114
$H_2O-CH_3\cdot OH$	0·00537
$H_2O-C_2H_5\cdot OH$	0·00780
$H_2O-C_3H_7\cdot OH$	0·00900

FIG. 2.



The relatively great value for the last-mentioned pair is due to the lower stability of the complex, and the enhanced value of the viscosity itself at the maximum is explicable on two counts: (1) the larger molecular volume, (2) the greater asymmetry of the complex.

PHYSICAL CHEMISTRY LABORATORY,
 TECHNICAL COLLEGE,
 EAST HAM.

CLXXVI.—*Studies on the Cobaltinitrites.*

By MARY CUNNINGHAM and FREDERICK MOLLWO PERKIN.

Cobaltinitrites of Organic Amines.

As ammonium and potassium cobaltinitrites are very insoluble salts and are readily prepared by the interaction of ammonium or potassium salts respectively and sodium cobaltinitrite, it seemed that in all probability primary amines would react in a similar manner, and it also appeared likely that there would be a difference in the action of primary, secondary, and tertiary amines, in which case sodium cobaltinitrite could be employed as a reagent for distinguishing between the different classes of amines. Indeed, it was found that when a concentrated solution of a salt of a primary amine was added to a concentrated solution of sodium cobaltinitrite, a crystalline compound was precipitated having the formula $(\text{Alk}\cdot\text{NH}_3)_3\text{Co}(\text{NO}_2)_6$. The compounds, however, are not very stable, and must be removed from the mother liquor, washed, and dried on a porous plate as quickly as possible. Secondary amines of the aliphatic series give a similar precipitate, but as a rule they are much more soluble, and consequently very highly concentrated solutions both of the amine and sodium cobaltinitrite must be employed; it is also advantageous to cool the solutions with ice. Tertiary amines, as might be expected, have no action.

With aromatic amines the reaction is rather different, the primary aromatic amines giving compounds which have the general formula $(\text{Ph}\cdot\text{NH}_3)_3\text{Co}(\text{NO}_2)_6$. Generally speaking, they are much less stable than the compounds produced with the aliphatic amines. Secondary aromatic amines yield a precipitate which almost immediately decomposes, a nitroso-compound being formed. With methylaniline, nitrosomethylaniline is produced, and dimethylaniline yields *p*-nitrosodimethylaniline, so that, in the case of the aromatic series, we really have a method for distinguishing between primary, secondary, and tertiary amines.

Inorganic Cobaltinitrites.

Potassium cobaltinitrite is one of the longest known of the cobaltinitrites, but there appears some little doubt as to its actual composition when prepared by the addition of a solution of a potassium salt to a solution of sodium cobaltinitrite, the formula being variously given as $\text{K}_3\text{Co}(\text{NO}_2)_6$, and $\text{NaK}_2\text{Co}(\text{NO}_2)_6\cdot\text{H}_2\text{O}$.

Rosenheim and Koppel (*Zeitsch. anorg. Chem.*, 1898, **17**, 42),

who prepared it under conditions in which there could be no sodium present, by suspending pure cobalt carbonate in a small quantity of water, adding the calculated quantity of potassium hydroxide, carbonate, or nitrite, and then passing in nitrogen trioxide prepared from arsenious oxide and nitric acid, obtained a compound having the formula $K_3Co(NO_2)_6$. Adie (Trans., 1900, 77, 1076) added a potassium salt to a solution of sodium cobaltinitrite, and obtained a compound to which he gave the formula $K_2NaCo(NO_2)_6 \cdot H_2O$. None of these authors, however, started with the pure sodium salt, but we have succeeded in preparing pure sodium cobaltinitrite, and analysis showed it to possess the formula $Na_3Co(NO_2)_6$.

Experiments were then undertaken, employing this pure product as starting material, in order to ascertain whether potassium cobaltinitrite is the tripotassium salt or the dipotassium sodium compound. We find that if excess of a potassium salt is present, the tripotassium cobaltinitrite, $K_3Co(NO_2)_6$, is formed, but that with excess of sodium cobaltinitrite the salt $K_2NaCo(NO_2)_6$ is produced; when neither is in considerable excess the analytical figures show that frequently a mixture of the two salts is obtained.

Apparently Adie (*loc. cit.*) always employed an excess of the sodium salt, a solution of which he prepared, but did not isolate the solid compound, and this accounts for his analytical numbers. The salts obtained by us did not, as a rule, contain water of crystallisation.

We do not consider that the precipitation of potassium cobaltinitrite is a method which can be recommended for the analysis of potassium or cobalt compounds. In the first place, the precipitate may be a mixture of the tri- and di-potassium salts. Secondly, the potassium salt is extremely difficult to wash. It will, in the first place, settle fairly well, and can easily be washed once by decantation. On filling up the vessel with water, however, the precipitate settles only slowly. On the third washing, it settles still less satisfactorily, and shows a strong tendency to become colloidal. Finally, it becomes almost an impossibility to filter it satisfactorily. Adie (*loc. cit.*) also refers to the difficulty of obtaining a clear filtrate, although he recommends the use of the salt in analysis.

We have also prepared and analysed silver cobaltinitrite; this substance, according to Rosenheim and Koppel (*Zeitsch. anorg. Chem.*, 1898, 17, 43), is not formed by the addition of sodium cobaltinitrite to silver salts, silver nitrite being produced.

Lead cobaltinitrite has also been prepared, and we find that when freshly precipitated it contains varying amounts of water of crystallisation, which, however, are gradually lost when it is kept

in a desiccator over phosphoric oxide until it finally contains four molecular proportions.

Thallium cobaltinitrite has the formula $Tl_3Co(NO_2)_6$.

EXPERIMENTAL.

Methylamine Cobaltinitrite, $(CH_3 \cdot NH_3)_3Co(NO_2)_6$.

To a nearly saturated solution of methylamine hydrochloride an excess of a nearly saturated solution of pure sodium cobaltinitrite was added. Almost immediately a deep yellow, crystalline precipitate was produced. After stirring for three or four minutes, it was collected by the aid of the pump and rapidly washed with a very small quantity of ice-cold water and then with 50 per cent. alcohol. It was then spread on a porous plate, from which it was removed in the course of an hour or so and placed in an evacuated desiccator over sulphuric acid or phosphoric oxide. The yellow powder so obtained is quite stable when kept free from moisture, but in presence of even a trace it slowly decomposes with evolution of nitrous fumes, forming a red, pasty mass; this contains a small quantity of an oily liquid, which has an odour rather resembling that of nitromethane, and may possibly be this substance, but the quantities obtained were too small to examine. On heating, the substance gradually decomposes and shows no definite melting point. Methylamine cobaltinitrite is extremely soluble in water, and is at once decomposed by organic solvents. It can, however, be precipitated in presence of acetic acid. It decomposes violently with strong mineral acids; dilute acids decompose it with evolution of nitrous fumes.

For analysis, a weighed quantity was moistened with concentrated sulphuric acid and heated until all the nitrous fumes were driven off. To drive off all the nitrous fumes, it is necessary to heat until fumes of sulphuric acid are also evolved. The cobalt was then deposited electrolytically. A platinum gauze cathode and rotating anode were employed, and the cobalt was deposited in about half an hour.

Before electrolysis, the acid solution was diluted with water, rendered faintly alkaline with ammonia, then faintly acid with phosphoric acid, and about 5 grams of sodium dihydrogen phosphate were added. It was found that if the nitrite was not completely decomposed, the electrolysis required several hours, and the results were not satisfactory:

Found, Co = 13.57.

$C_3H_{18}O_{12}N_9Co$ requires Co = 13.68 per cent.

Ethylamine Cobaltinitrite,* $(C_2H_5 \cdot NH_3)_3Co(NO_2)_6$.

This was prepared in a similar manner to that adopted in the previous case. It consists of small, glistening, orange-coloured needles, and in properties closely resembles the methylamine compound:

Found, Co = 12.80.

$C_6H_{24}O_{12}N_9Co$ requires Co = 12.47 per cent.

Diethylamine Cobaltinitrite, $[(C_2H_5)_2NH_2]_3Co(NO_2)_6$.

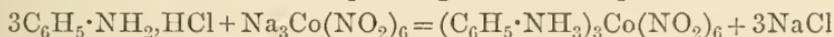
Diethylamine hydrochloride reacts with a concentrated solution of sodium cobaltinitrite, yielding an orange-yellow, crystalline compound, which is very similar in properties to the cobaltinitrites of the primary amines. It is, however, readily soluble in acetic acid, whereas the primary cobaltinitrites are not:

Found, Co = 10.62.

$C_{12}H_{36}O_{12}N_9Co$ requires Co = 10.59 per cent.

Aniline Cobaltinitrite, $(C_6H_5 \cdot NH_3)_3Co(NO_2)_6$.

Owing to its extreme instability in presence of water, this substance is much more difficult to prepare than the cobaltinitrites of the aliphatic amines. Quantities of aniline hydrochloride and sodium cobaltinitrite corresponding with the equation:



were dissolved separately in as little ice-cold water as possible. The solutions were then mixed in a beaker surrounded with ice, stirred for a few minutes, and filtered as quickly as possible. The product, after being washed with a little ice-cold water, was transferred to a porous plate and placed in a desiccator. When dry, it was removed from the porous plate and kept in a desiccator over phosphoric oxide. Even when working in this rapid manner it is not always possible to prevent the compound decomposing; if, however, it is once quite dry, it will keep for some time.

The product is a yellow, crystalline powder, which becomes black in a few days even when kept in a desiccator. It is fairly readily soluble in water, but cannot be recrystallised from this solvent. All organic solvents decompose it. If attempts are made to wash the substance with alcohol or ether a tarry product is produced.

Very considerable difficulty was experienced in analysing this

* This substance has already been prepared by K. A. Hofmann and O. Burger (*Ber.*, 1907, **40**, 3293) by suspending cobalt carbonate in water, adding ethylamine, and passing in nitrogen trioxide.

substance, because concentrated sulphuric acid decomposes it with extreme violence, and dilute sulphuric acid has very little action on it, except when boiled with it for some time, and then the tarry products produced make it difficult to filter the solution. The most suitable method was found to be to mix the substance with dilute sulphuric acid, and then to add concentrated acid drop by drop. This prevented explosive decomposition, and the substance dissolved with a deep red coloration. The solution was then rendered strongly alkaline with ammonia, sodium dihydrogen phosphate added, and a few drops of 10 per cent. phosphoric acid to make the solution faintly acid. It was then electrolysed, using a rotating anode and a gauze cathode. With a current of about two amperes, the deposition was complete in about half an hour :

Found, C=34.92; H=4.78; N=20.21; Co=9.41.

$C_{18}H_{24}O_{12}N_9Co$ requires C=35.00; H=3.89; N=20.42; Co=9.56 per cent.

p-Toluidine Cobaltinitrite, $(CH_3 \cdot C_6H_4 \cdot NH_3)_3Co(NO_2)_6$.

This substance was prepared in a similar manner to the aniline compound. It forms orange-yellow needles, and resembles the aniline compound in properties. It was analysed, with the following result :

Found, Co=9.49.

$C_{21}H_{30}O_{12}N_9Co$ requires Co=8.95 per cent.

p-Bromoaniline Cobaltinitrite, $(C_6H_4Br \cdot NH_3)_3Co(NO_2)_6$.

This compound is much more stable than either of the preceding. It is an orange-yellow substance, forming needle-shaped crystals, which are only sparingly soluble in water; there is consequently no difficulty in washing it. It is decomposed by organic solvents, but can be kept for weeks in a desiccator without decomposition. When added to concentrated sulphuric acid it inflames :

Found, Co=6.68.

$C_{18}H_{21}O_{12}N_9Br_3Co$ requires Co=6.91 per cent.

The nitroanilines give no precipitate with sodium cobaltinitrite; probably they do not react owing to their negative character.

Methylaniline.—When a concentrated solution of methylaniline hydrochloride is cooled in ice and a similarly cooled solution of sodium cobaltinitrite added to it, a yellow precipitate is produced, which, however, almost immediately decomposes with the formation of an oil. The decomposition is so rapid that it is not possible to collect the substance. The oil was extracted with ether, and the

ethereal solution well washed with water and aqueous sodium carbonate; on evaporating the ether, a yellow oil was obtained which gave Liebermann's reaction; it was therefore a nitroso-compound.

This decomposition of the cobaltinitrite with formation of the nitroso-compound was not noticed with the aliphatic secondary amines.

Dimethylaniline.—On adding a concentrated solution of dimethylaniline in acetic acid to an aqueous solution of sodium cobaltinitrite, a dirty yellow precipitate is formed, which, on rendering the solution alkaline with sodium carbonate, gives a deep green solution. If this solution is extracted with ether and the ethereal solution evaporated, crystals of *p*-nitrosodimethylaniline are produced.

Potassium Cobaltinitrite.

On adding an excess of a solution of sodium cobaltinitrite to a solution of a potassium salt, a canary-yellow precipitate is at once produced. This rapidly settles, but is very difficult to wash free from sodium salts, owing to its tendency to become colloidal. The well-washed substance was spread on a porous plate, and, when dry, placed in an evacuated desiccator over sulphuric acid for twenty-four hours. For analysis the substance was treated with a small quantity of concentrated sulphuric acid, and heated in a platinum basin until white fumes of sulphuric acid were evolved. It was then cooled, water added, and, after the addition of excess of ammonia, electrolysed.

The potassium was estimated by treating a separate portion with hydrochloric acid and precipitating as potassium platinichloride. This method was found to be more satisfactory than evaporating the electrolysed solution to dryness and expelling the ammonium salts by ignition.

It has already been mentioned on p. 1563 that the constitution of the potassium salt varies, depending on whether the sodium cobaltinitrite or the potassium salt is in excess.

The following analyses, taken from a large number of determinations, bear this out. In the first case, the potassium salt was in excess. In the second case, an excess of the sodium salt was present, and in the third and fourth cases the proportions were about equal; these last show that the substance obtained was a mixture of tripotassium cobaltinitrite and of dipotassium sodium cobaltinitrite:

I. Found, Co=13·25; K=25·55.

$K_3Co(NO_2)_6$ requires Co=13·05; K=25·88 per cent.

II. Found, Co=(i) 13·7, (ii) 13·6; K=17·78.

$K_2NaCo(NO_2)_6$ requires Co=13·53; K=17·88 per cent.

III. Found, K=19·77.

IV. Found, K=20·71.

Sodium Cobaltinitrite.

Sodium nitrite (150 grams) is dissolved in hot water (150 c.c.), and the solution cooled to about 45° to 50°, when cobalt nitrate (50 grams) is added, and the mixture stirred until the salt has dissolved. Glacial acetic acid (25 c.c.) is now added, and after thoroughly shaking, the mixture is kept for twenty minutes. If necessary, it is filtered from traces of potassium cobaltinitrite, due to the presence of potassium salt in the sodium nitrite. A rapid current of air is then aspirated through the filtrate for half an hour to remove oxides of nitrogen, and then 95 per cent. alcohol (150 c.c.) is added, the solution being shaken during the addition. It is then shaken occasionally for an hour, and the voluminous precipitate of sodium cobaltinitrite collected with the aid of the pump. It is then washed once with a small quantity of 60 per cent. alcohol, and two or three times with 95 per cent. alcohol, and finally dried on a porous plate. The yield is about 60 per cent. of the theoretical. An analysis of the air-dried product showed it to have the composition $Na_3Co(NO_2)_6$:

Found, Co=14·41; Na=16·98.

$Na_3Co(NO_2)_6$ requires Co=14·52; Na=17·09 per cent.

In Dammer's *Handbuch* (Vol. 4), the formula is given as $Na_3Co(NO_2)_6, 2\frac{3}{4}H_2O$, but in all probability the substance had not been properly dried before analysis, or it may be that washing with alcohol, as we find advisable, removes water of crystallisation, which would otherwise be present. The compound is a pale orange-yellow, crystalline powder, extremely soluble in water, from which, however, it can be reprecipitated by the addition of much alcohol.

Silver Cobaltinitrite.

On adding a solution of silver nitrate to a concentrated solution of sodium cobaltinitrite, an orange-yellow precipitate is produced. This salt is fairly soluble in water, and was therefore purified by washing it with 50 per cent. alcohol. For analysis, the salt was decomposed with nitric acid, the silver precipitated as chloride, which was washed, dissolved in potassium cyanide, and the silver deposited electrolytically. The solution containing the cobalt was evaporated to dryness, treated with sulphuric acid, and heated to

expel nitric acid. It was then diluted, rendered alkaline with ammonia, and electrolysed:

Found, Ag=49.08; Co=9.00.

$\text{Ag}_3\text{Co}(\text{NO}_2)_6$ requires Ag=49.14; Co=8.95 per cent.

Thallium Cobaltinitrite.

This, prepared by mixing solutions of thallium carbonate and sodium cobaltinitrite, is bright scarlet. It has already been described by Jørgensen (*Zeitsch. anorg. Chem.*, 1894, **5**, 146), but as, apparently, it was not analysed, we estimated the thallium electrolytically. The compound was decomposed with nitric acid and electrolysed, using a mercury cathode and a rotating anode:

Found, Tl=64.4; Co=6.12.

$\text{Tl}_3\text{Co}(\text{NO}_2)_6$ requires Tl=64.62; Co=6.23 per cent.

Lead cobaltinitrite is easily prepared by adding a solution of a lead salt to a solution of sodium cobaltinitrite. It is an orange-yellow, semi-crystalline powder, which is very sparingly soluble in water. The substance was analysed by decomposing it with nitric acid, and the solution made up so that it contained about 30 per cent. of nitric acid. It was then electrolysed, using a roughened platinum dish as anode, and weighed as lead peroxide. We had great difficulty in obtaining concordant results, but we found that this was due to the fact that when freshly precipitated it contained variable quantities of water, which, however, was gradually lost when the compound was kept in a desiccator over phosphoric oxide, until finally it contained $4\text{H}_2\text{O}$. Rosenheim and Koppel (*Zeitsch. anorg. Chem.*, 1898, **17**, 48) found $12\text{H}_2\text{O}$ in a specimen prepared by them. We have analysed samples containing about $11\text{H}_2\text{O}$, but we never obtained one with $12\text{H}_2\text{O}$. The following figures were obtained with samples which had been dried for from two to three days in a desiccator containing phosphoric oxide:

Found, Pb=(i) 44.91, (ii) 44.78.

$\text{Pb}_3[\text{Co}(\text{NO}_2)_6]_2 \cdot 4\text{H}_2\text{O}$ requires Pb=45.56 per cent.

When solutions of sodium cobaltinitrite are added to concentrated solutions of carbamide, nitrogen is evolved. With hydroxylamine, the evolution of nitrogen is very rapid. With semicarbazide, ammonium cobaltinitrite is precipitated.

CHEMICAL DEPARTMENT,
BOROUGH POLYTECHNIC INSTITUTE,
LONDON, S.E.

CLXXVII.—*The Effect of Contiguous Unsaturated Groups on Optical Activity. Part II. Acids containing Two Adjacent Ethenoid Groups.*

By THOMAS PERCY HILDITCH (1851 Exhibition Scholar).

IN continuation of the scheme outlined in the first communication of this series (Trans., 1909, 95, 331), the author has examined some optically active derivatives containing the unsaturated system



A considerable number of compounds have been utilised, in which, on the one hand, the optically active part of the molecule, and on the other, the groups adjacent to the conjugated ethenoid system, have been varied. The corresponding reduction products have also been prepared, and since in all cases the rotatory power of the conjugated derivative varies in the same manner with respect to the reduced compounds, it follows that the constant effect produced must be due to the adjacent ethylenic groups, the only system which remains unchanged throughout the examples studied.

An objection to the use of carboxylic acids lies in the fact that an unsaturated carboxyl residue must invariably intervene between the optically active alcohol or base and the studied unsaturated system, and possibly exert varying effects in different instances, but this failing may to a great extent be overcome by consideration of the rotatory power of the reduced esters or salts.

Four different series of acids were used, namely:

- (a) Sorbic acid, $\text{CHMe}:\text{CH}:\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$, etc.;
- (b) Muconic acid, $\text{CO}_2\text{H}\cdot\text{CH}:\text{CH}:\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$, etc.;
- (c) Piperic acid, $\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}:\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$, etc.; and
- (d) Cinnamylidenemalonic acid, $\text{CHPh}:\text{CH}:\text{CH}:\text{C}(\text{CO}_2\text{H})_2$, etc.

In most cases all the possible reduced acids were also utilised, including the $\alpha\beta$ -dihydro-acids, the $\beta\gamma$ -dihydro-acids, and the fully reduced acids, $\text{R}\cdot[\text{CH}_2]_4\cdot\text{CO}_2\text{H}$.

Menthol and brucine served as the sources of optical activity, and, in order to obtain an idea of the normal molecular rotatory power of menthyl esters and brucine salts, use has been made of the principle laid down by Guye (*Compt. rend.*, 1894, 119, 906), Tschugaeff (*Ber.*, 1898, 31, 360), and Minguin (*Bull. Soc. chim.*, 1902, [iii], 27, 593) that the molecular rotation of active derivatives of an homologous series, such as the normal fatty acids, attains a constant value, and the mean value of the menthyl esters and brucine salts of acetic to *n*-hexoic acid has been adopted as the normal value in each case.

These numbers, deduced from measurements made by the author in the same solvent (chloroform) and at the same concentrations and temperature (15°) as the main results, are given in the following table :

Acid.	Menthyl ester.		Brucine salt.	
	5 per cent.	2½ per cent.	5 per cent.	2½ per cent.
Acetic.....	-158·2	-157·0	-258·0	-260·6
Propionic	156·6	157·2	248·1	252·3
n-Butyric	161·2	161·7	247·4	251·2
n-Valeric	161·9	162·1	247·4	251·6
n-Hexaic	164·4	168·1	246·8	252·8
Mean value ...	-160·46	-161·22	-249·54	-253·70

It may be pointed out that the menthyl ester values agree well with those of Tschugaeff (*loc. cit.*) measured without solvent, and those of Rupe (*Annalen*, 1903, 327, 164) determined in alcoholic solution.

EXPERIMENTAL.

The three unsaturated acids of the muconic acid group were prepared from the dimethyl ester of $\beta\gamma$ -hydromuconic acid as described by Bode (*Annalen*, 1864, 132, 95), Ruhemann (*Trans.*, 1890, 57, 931), and Baeyer and Rupe (*Annalen*, 1890, 256, 7). Adipic acid was obtained by the oxidation of cyclohexanol (Holleman, van der Laar, and Slyper *Rec. trav. chim.*, 1905, 24, 23).

The $\beta\gamma$ -hydro-acids and piperonylbutyric acid were prepared from sorbic, piperic, and cinnamylidenemalononic acids by reduction with sodium amalgam, and the $\beta\gamma$ -acids were converted into the $\alpha\beta$ -isomerides by Riiber's method (*Ber.*, 1904, 37, 3120).

I. Menthyl Esters.

The menthyl esters used were prepared, except when otherwise stated, by acting on the acid with a slight excess of thionyl chloride, warming on the water-bath, and finally distilling off excess of this reagent under diminished pressure. The resulting acid chloride was mixed with rather more than the theoretical amount of menthol, and heated at 100° for five or six hours. After cooling, the mass was dissolved in ether and shaken once or twice with dilute sodium carbonate solution. The ethereal extract was evaporated, and the ester purified by distillation under diminished pressure or by recrystallisation.

Dimenthyl Muconate, $C_{10}H_{19}\cdot CO_2\cdot CH\cdot CH\cdot CH\cdot CH\cdot CO_2\cdot C_{10}H_{19}$.—This ester separated from methyl alcohol in well defined, tetrahedral crystals, which possessed the unusually high melting point (for an ester of menthol) of 168° :

0.1719 gave 0.4689 CO₂ and 0.1547 H₂O. C = 74.40; H = 10.00.

C₂₆H₄₂O₄ requires C = 74.64; H = 10.05 per cent.

Dimethyl βγ-Hydromuconate,

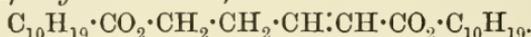


—In order to eliminate the possibility of any αβ-acid being formed in consequence of the presence of hydrogen chloride, the βγ-acid was heated in a sealed tube at 130° with excess of menthol for ten hours. In this way a rather poor yield of the ester was obtained. After purification from methyl alcohol, it formed soft, rhombohedral crystals, readily soluble in the usual organic solvents, and melting at 79°:

0.1328 gave 0.3629 CO₂ and 0.1238 H₂O. C = 74.54; H = 10.36.

C₂₆H₄₄O₄ requires C = 74.30; H = 10.48 per cent.

Dimethyl αβ-Hydromuconate,



—This ester was obtained in much better yield than either of the foregoing. It was recrystallised from light petroleum, and then formed radiating needles, soluble in most of the ordinary solvents, and melting at 83°:

0.1237 gave 0.3359 CO₂ and 0.1137 H₂O. C = 74.07; H = 10.22.

C₂₆H₄₄O₄ requires C = 74.30; H = 10.45 per cent.

Dimethyl Adipate, C₁₀H₁₉ · CO₂ · CH₂ · CH₂ · CH₂ · CH₂ · CO₂ · C₁₀H₁₉.

—This ester was prepared from adipic acid (8 grams). Yield 11 grams. The substance crystallised from light petroleum in small, wax-like needles, melting at 61°:

0.1071 gave 0.2918 CO₂ and 0.1040 H₂O. C = 74.30; H = 10.79.

C₂₀H₄₀O₄ requires C = 73.92; H = 10.90 per cent.

Menthyl Piperate, CH₂ · O₂ · C₆H₃ · CH : CH · CH : CH · CO₂ · C₁₀H₁₉.—This was obtained in small, colourless needles, melting at 83°. It is readily soluble in organic media, and was recrystallised from a small amount of methyl alcohol:

0.1096 gave 0.2984 CO₂ and 0.0796 H₂O. C = 74.25; H = 8.07.

C₂₂H₃₈O₄ requires C = 74.16; H = 7.86 per cent.

Menthyl βγ-Hydropiperate,

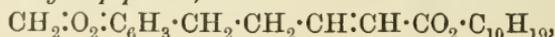


was prepared by heating the acid and menthol alone at about 130° for a day. The compound was purified by distillation under diminished pressure, the portion boiling constantly at 263°/25 mm. being taken as pure. The ester is a readily soluble, pale yellow oil:

0.1552 gave 0.4176 CO₂ and 0.1136 H₂O. C = 73.36; H = 8.13.

C₂₂H₃₀O₄ requires C = 73.74; H = 8.38 per cent.

Menthyl αβ-Hydropiperate,



boiled at 270—273°/25 mm. It solidifies in a freezing mixture, but at the ordinary temperature is a colourless oil, which gradually resinifies in air :

0·1237 gave 0·3348 CO₂ and 0·0916 H₂O. C = 73·82 ; H = 8·23.

C₂₂H₃₀O₄ requires C = 73·74 ; H = 8·38 per cent.

Menthyl Piperonylbutyrate,

CH₂:O₂:C₆H₃:CH₂:CH₂:CH₂:CH₂:CO₂:C₁₀H₁₉.

—This is best prepared by heating the acid with a slight excess of menthol at 130° for about fifteen hours, after the reaction mixture has been saturated in the cold with dry hydrogen chloride. It is a colourless oil, not very stable in air, but boiling (practically undecomposed) at 248—251°/20 mm. :

0·1402 gave 0·3744 CO₂ and 0·1148 H₂O. C = 72·85 ; H = 9·10.

C₂₂H₃₂O₄ requires C = 73·33 ; H = 8·89 per cent.

II. *Brucine Salts.*

The rotations of the brucine salts were directly obtained by mixing exact equivalent amounts of anhydrous brucine and the various acids in dry chloroform and making up to the required concentration. The salts were then recovered from the chloroform solution and purified for analysis and characterisation by recrystallisation from various solvents.

Dibrucine Muconate, C₆H₆O₄(C₂₃H₂₆O₄N₂)₂, 8H₂O.—Small, hard, radiating prisms, sparingly soluble in acetone, moderately so in water or chloroform, and melting indefinitely at 164—168° :

0·1228 gave 0·2604 CO₂ and 0·0714 H₂O. C = 57·81 ; H = 6·46.

0·1382 lost 0·0183 H₂O at 100°. H₂O = 13·24.

C₅₂H₅₈O₁₂N₄, 8H₂O requires C = 58·09 ; H = 6·88 ; H₂O = 13·41 per cent.

Dibrucine βγ-Hydromuconate, C₆H₈O₄(C₂₃H₂₆O₄N₂)₂, 8H₂O.—White, cubical crystals, readily soluble in water, and melting to a clear liquid at 113° :

0·1320 gave 0·2812 CO₂ and 0·0848 H₂O. C = 58·09 ; H = 7·14.

0·1887 lost 0·0244 H₂O at 100°. H₂O = 12·93.

C₅₂H₆₀O₁₂N₄, 8H₂O requires C = 57·98 ; H = 7·06 ; H₂O = 13·39 per cent.

Dibrucine αβ-Hydromuconate, C₆H₈O₄(C₂₃H₂₆O₄N₂)₂, 5½H₂O.—Small, white octahedra, slightly soluble in acetone, and moderately so in chloroform, melting at 166° :

0·1482 gave 0·3291 CO₂ and 0·0862 H₂O. C = 60·54 ; H = 6·46.

0·1854 lost 0·0179 H₂O at 100°. H₂O = 9·66.

C₅₂H₆₀O₁₂N₄, 5½H₂O requires C = 60·53 ; H = 6·31 ; H₂O = 9·60 per cent.

Dibrucine Adipate, C₆H₁₀O₄(C₂₃H₂₆O₄N₂)₂.—Soft, white tablets, readily soluble in cold water, and melting and decomposing at 204° :

0.1108 gave 0.2712 CO₂ and 0.0654 H₂O. C = 66.74; H = 6.56.

C₅₂H₆₂O₁₂N₄ requires C = 66.82; H = 6.64 per cent.

Brucine Piperate, C₁₂H₁₀O₄, C₂₃H₂₆O₄N₂, 1½H₂O.—Long, thin, rectangular tablets from water, melting at 144°:

0.1576 gave 0.3786 CO₂ and 0.0824 H₂O. C = 65.52; H = 5.81.

0.1959 lost 0.0085 H₂O at 100°. H₂O = 4.34.

C₃₅H₃₆O₈N₂, 1½H₂O requires C = 65.72; H = 6.10; H₂O = 4.23 per cent.

Brucine βγ-Hydropiperate, C₁₂H₁₂O₄, C₂₃H₂₆O₄N₂, 3H₂O.—Slender, slightly efflorescent prisms, which crystallise well from water, and melt at 73°:

0.0914 gave 0.2109 CO₂ and 0.0505 H₂O. C = 62.92; H = 6.18.

C₃₅H₃₈O₈N₂, 3H₂O requires C = 62.87; H = 6.59 per cent.

Brucine αβ-Hydropiperate, C₁₂H₁₂O₄, C₂₃H₂₆O₄N₂, 4H₂O.—Quadratic tablets, melting at 70°, and frothing and evolving water of crystallisation at 100°:

0.1219 lost 0.0126 H₂O at 100°. H₂O = 10.34.

C₃₅H₃₈O₈N₂, 4H₂O requires H₂O = 10.50 per cent.

Brucine Piperonylbutyrate, C₁₂H₁₄O₄, C₂₃H₂₆O₄N₂, 4½H₂O.—Fine, soft needles, melting at 73—75° to a clear liquid. The salt dried at 100° was used for analysis:

0.1203 gave 0.2997 CO₂ and 0.0686 H₂O. C = 67.79; H = 6.34.

0.1363 lost 0.0160 H₂O at 100°. H₂O = 11.74.

C₃₅H₄₀O₈N₂ requires C = 68.17; H = 6.49; 4½H₂O = 11.62 per cent.

Brucine Sorbate, C₆H₈O₂, C₂₃H₂₆O₄N₂, 1½H₂O.—Hard, compact prisms, melting at 167°:

0.1204 gave 0.2900 CO₂ and 0.0768 H₂O. C = 65.69; H = 7.09.

0.2387 lost 0.0120 H₂O at 100°. H₂O = 5.03.

C₂₉H₃₄O₆N₂, 1½H₂O requires C = 65.30; H = 6.94; H₂O = 5.07 per cent.

Brucine βγ-Hexenoate, C₆H₁₀O₂, C₂₃H₂₆O₄N₂.—Stout prisms, darkening at 175°, and melting at 183°.

Brucine n-Hexoate, C₆H₁₂O₂, C₂₃H₂₆O₄N₂, 3H₂O.—Slightly deliquescent, cubical crystals, melting at 66°:

0.1186 gave 0.2684 CO₂ and 0.0808 H₂O. C = 61.70; H = 7.57.

C₂₉H₃₈O₆N₂, 3H₂O requires C = 61.70; H = 7.80 per cent.

Dibrucine Cinnamylidenemalonate, C₁₂H₁₀O₄, C₄₆H₅₂O₈N₄, 5H₂O.—A cream-coloured powder, very soluble in water, frothing and decomposing at 110°:

0.1808 gave 0.4212 CO₂ and 0.1076 H₂O. C = 63.52; H = 6.62.

C₅₈H₆₂O₁₂N₄, 5H₂O requires C = 63.49; H = 6.57 per cent.

Dibrucine Phenylpropenylmalonate, C₁₂H₁₂O₄, C₄₆H₅₂O₈N₄, 4H₂O.—A mass of soft, cream crystals, melting and frothing at 96—99°:

0.1634 gave 0.3876 CO₂ and 0.0944 H₂O. C = 64.71; H = 6.47.

C₅₈H₆₄O₁₂N₄·4H₂O requires C = 64.45; H = 6.67 per cent.

Dibrucine Phenylpropylidenemalonate, C₁₂H₁₂O₄·C₄₀H₅₂O₈N₄·3H₂O.
—Small, monoclinic prisms, melting at 68°, and evolving water of crystallisation at 105°:

0.1800 gave 0.4338 CO₂ and 0.1266 H₂O. C = 65.73; H = 6.50.

C₅₃H₆₄O₁₂N₄·3H₂O requires C = 65.54; H = 6.59 per cent.

Polarimetric Results.

The polarimetric measurements were carried out, as in previous investigations, in chloroform solution in a 2-dcm. tube, and, in the majority of cases, at two concentrations. The temperature of the solutions did not vary beyond the limits of 14.5° to 16°.

The brucine was dried to constant weight at 100° in order to remove water of crystallisation. The rotations before use (5 per cent. solution in chloroform) were then as follows:

	[α] _D .	[M] _D .
Menthol	-48.84°	-76.2°
Brucine	121.50	478.6

The results obtained are collected in the following tables, which give, in addition to the specific and molecular rotatory powers, the difference between the molecular rotation of each compound and the normal values previously quoted:

I. Menthyl Esters.

(a) Muconic Acid Series:

	Percentage concentration.					
	5.			2½.		
	[α] _D .	[M] _D .	Diff.	[α] _D .	[M] _D .	Diff.
Dimethyl muconate	—	—	—	-93.40°	-390.4°	68.0°
„ αβ-hydromuconate ...	-88.80°	-372.9°	52.0°	88.78	372.8	50.4
„ βγ-hydromuconate ...	81.52	342.4	21.5	80.78	339.3	16.9
„ adipate	83.80	353.6	32.7	83.60	352.8	30.4

(b) Piperic Acid Series:

Menthyl piperate	-53.02°	-188.8°	28.3°	-52.76°	-187.8°	26.6°
„ αβ-hydropiperate	45.92	164.4	3.9	46.08	165.0	3.8
„ βγ-hydropiperate	42.22	151.1	-9.4	42.12	150.8	-10.4
„ piperonylbutyrate	39.68	142.9	-17.6	38.00	136.8	-24.4

II. Brucine Salts.

(a) Muconic Acid Series:

Dibrucine muconate	-9.52°	-88.5°	410.6°	-9.72°	-90.4°	417.0°
„ αβ-hydromuconate	38.04	354.6	144.5	38.52	359.0	148.4
„ βγ-hydromuconate	38.50	358.3	140.3	38.24	356.5	150.9
„ adipate	42.80	399.2	99.9	42.60	397.8	109.6

II. *Brucine Salts* (continued).(b) *Piperic Acid Series* :

	Percentage concentration.					
	5.			2½.		
	[α] _D .	[M] _D .	Diff.	[α] _D .	[M] _D .	Diff.
Brucine piperate	-5.02°	-30.7°	218.8°	-4.68°	-28.6°	225.1°
,, $\alpha\beta$ -hydropiperate	25.10	154.1	95.4	25.12	154.3	99.4
,, $\beta\gamma$ -hydropiperate	29.08	178.5	71.0	29.16	179.1	74.6
,, piperonylbutyrate	28.26	174.1	75.4	27.68	170.5	83.2

(c) *Sorbic Acid Series* :

Brucine sorbate	-25.50°	-130.0°	119.5°	-23.84°	-120.6°	133.1°
,, hydrosorbate	44.72	227.2	22.3	42.16	214.2	39.5
,, <i>n</i> -hexoate	48.39	246.8	2.7	49.57	252.8	0.9

(d) *Cinnamylidenemalononic Acid Series* :

Dibrucine cinnamylidenemalonate	—	—	—	-9.84°	-98.99°	408.4°
,, $\alpha\beta$ -hydrocinnamylidenemalonate	-44.08°	-444.2°	54.9°	43.60	439.5	67.9
,, $\beta\gamma$ -hydrocinnamylidenemalonate	50.52	509.2	-10.1	50.12	505.2	2.2

It should be mentioned that Rupe (*loc. cit.*), in examining the effect caused by the proximity of the ethylenic bond to the asymmetric complex in the isomeric pentenoic, hexenoic, etc., menthyl esters, prepared menthyl sorbate and found that it possessed a much higher rotatory power than any of the mono-ethylenic esters, and assumed that the anomaly was due to the presence of the conjugated ethenoid system. It will be useful to compare these figures (obtained from alcohol solution) with the other series now recorded (the "differences" given are here calculated from Rupe's mean value for the fatty menthyl esters in alcohol, namely, $[M]_D = -164.6^\circ$).

	[M] _D .	Difference.
Menthyl sorbate	-221.3°	56.7°
,, $\alpha\beta$ -hexenoate	172.4	7.8
,, $\beta\gamma$ -hexenoate	164.1	-0.5
,, <i>n</i> -hexoate	164.7	0.1

It will be noticed that in the series studied by the author, the compounds containing two contiguous ethenoid groups possess, without exception, the greatest anomaly in their respective series, whilst in general the dihydro-acids possess a larger rotation than the fully saturated members. It should be observed that the effect produced by a conjugated system is very much better defined than those due to the $\alpha\beta$ - or $\beta\gamma$ -ethylenic acids; the rotatory powers of derivatives of the latter acids are relatively close to those of the saturated acids, and the differences between the isomeric $\alpha\beta$ - and $\beta\gamma$ -acids are usually of a small order, although, in all the instances examined, the $\alpha\beta$ -acid, the ethylenic linking of which is contiguous to the "unsaturated"

carboxyl group, and also lies nearer to the asymmetric system, possesses the larger anomaly (compare Rupe, *loc. cit.*). Finally, the rule that the saturated derivatives show least anomaly, finds an exception in the case of dimenthyl adipate, a point which is discussed in the next paper.

It is interesting, also, to notice the relative anomalies displayed by the different series studied. Muconic acid, for example, exhibits a larger anomaly than piperic acid both in menthyl ester and brucine salt; this is rather remarkable, in view of the great influence on optical activity which has been attributed to the phenyl group by many workers. It is most probably to be explained by the fact that muconic acid, $\text{CO}_2\text{H}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ (and its dimenthyl ester and dibrucine salt), possesses a structure which is symmetrical with respect to the centre of the conjugated system. The author has previously remarked (*Trans.*, 1908, **93**, 1620) that such a configuration is apparently favourable to the exhibition of quite abnormal rotatory power.

Again, the menthyl esters of two of the reduced piperic acids have values lying below the normal, in spite of the presence in the molecule of a benzenoid residue, and it must be conceded that, whilst that nucleus can undoubtedly produce marked effects on optical activity, numerous cases go to prove that there is a great deal of apparent irregularity which remains to be cleared up in the behaviour of this radicle.

In conclusion, emphasis must be laid on the much greater effect caused by the conjugation of two ethylenic groups than by that of an ethylenic and a carboxyl group together (as in the $\alpha\beta$ -hydro-acids). This result was to a certain extent to be expected, in view of Rupe's experience with menthyl sorbate, and of two instances of isomeric hydrocarbons previously quoted (Part I., this vol., p. 334), namely: $\Delta^{3:(8,9)}$ -*p*-menthadiene ($[\text{M}]_D + 133.6^\circ$, conjugated) and menthene ($[\text{M}]_D + 45.2^\circ$, unconjugated); phellandrene ($[\text{M}]_D + 82.1^\circ$, conjugated) and carvomenthene ($[\text{M}]_D - 2.9^\circ$, unconjugated).

The author wishes to express his indebtedness to Professor Knorr, in whose laboratory this work has been carried out, and to acknowledge the kind assistance of Mr. S. R. Edminson in connexion with several of the analyses.

UNIVERSITY OF JENA.

CLXXVIII.—*The Effect of Contiguous Unsaturated Groups on Optical Activity. Part III. The Normal Series of Fatty Dibasic Acids.*

By THOMAS PERCY HILDITCH (1851 Exhibition Scholar).

ATTENTION was drawn in the preceding communication to the fact that, whilst the menthyl esters and brucine salts of the saturated acids therein described possessed rotatory powers which as a rule were not greater than the "normal" molecular rotation of such esters or salts, those of adipic acid were found to be well in excess of the normal value. This exception appeared to be the more interesting, since of the various series of acids examined, adipic acid approached most nearly to a normal fatty acid.

In order to throw more light on this point, and also to examine the general effect of the progressive separation (by methylene groups) of the contiguous carboxyl groups in oxalic acid, the author has prepared the series of optically active esters and salts of the acids of this group from oxalic to sebacic inclusive. No complete series of such derivatives has previously been prepared; Walden (*J. Russ. Phys. Chem. Soc.*, 1898, 30, 767) gives values for the di-*l*-amyl esters of some of the acids, but unfortunately does not mention the adipic ester. His figures, too, were obtained from esters prepared from optically impure amyl alcohol.

The preparation and properties of the different compounds used in the investigation will be first described, and thereafter the details of the polarimetric measurements and the respective anomalies will be given. It should be emphasised that, in referring the differences to the mean value of the fatty acid derivatives as a standard, no particular importance is thereby attached to the use of these acids for this purpose. Nevertheless, since they are structurally the simplest organic acids, and since the rotatory power of their optically active derivatives attains a constant value, they are, in default of anything better, suitable as a standard of comparison. This method of estimating the anomaly in optical activity appears to the author to be preferable to the alternative of comparing the molecular rotatory power to that of the alcohol or alkaloid concerned, since the latter is usually of quite a different order, and, moreover, the direction of the change of rotation on esterification of different active alcohols (or salt-formation of active bases) by any inactive acid whatever is not always the same, even the sign of the rotation (as with amyl esters) being sometimes altered.

EXPERIMENTAL.

The *menthyl* esters were obtained by the thionyl chloride method described in the preceding paper.

Dimenthyl Oxalate, $(\text{CO}_2 \cdot \text{C}_{10}\text{H}_{19})_2$.—Firm, white octahedra, which melted at 67° (compare Zelikoff, *Ber.*, 1904, 37, 1374):

0.1364 gave 0.3578 CO_2 and 0.1252 H_2O . C = 71.53; H = 10.20.

$\text{C}_{22}\text{H}_{38}\text{O}_4$ requires C = 72.13; H = 10.39 per cent.

Dimenthyl Malonate, $\text{H}_2(\text{CO}_2 \cdot \text{C}_{10}\text{H}_{19})_2$.—Seven grams of soft, slender needles were obtained from 4 grams of acid and 12 grams of menthol; the ester crystallises well from methyl alcohol, and melts at 62° :

0.1446 gave 0.3850 CO_2 and 0.1326 H_2O . C = 72.61; H = 10.20.

$\text{C}_{23}\text{H}_{40}\text{O}_4$ requires C = 72.63; H = 10.53 per cent.

Dimenthyl Succinate, $\text{C}_{10}\text{H}_{19} \cdot \text{CO}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2 \cdot \text{C}_{10}\text{H}_{19}$.—Colourless, rhombic crystals, melting at 63° (compare Arth, *Ann. Chim. Phys.*, 1886, [vi], 7, 438):

0.1034 gave 0.2759 CO_2 and 0.0996 H_2O . C = 72.76; H = 10.70.

$\text{C}_{24}\text{H}_{42}\text{O}_4$ requires C = 73.10; H = 10.66 per cent.

Dimenthyl Glutarate, $\text{C}_{10}\text{H}_{19} \cdot \text{CO}_2 \cdot [\text{CH}_2]_3 \cdot \text{CO}_2 \cdot \text{C}_{10}\text{H}_{19}$.—This compound formed a colourless oil, boiling at $240\text{--}243^\circ/20$ mm., which slowly crystallised to a mass of colourless needles:

0.1260 gave 0.3386 CO_2 and 0.1210 H_2O . C = 73.28; H = 10.68.

$\text{C}_{25}\text{H}_{44}\text{O}_4$ requires C = 73.52; H = 10.78 per cent.

Dimenthyl Pinelate, $\text{C}_{10}\text{H}_{19} \cdot \text{CO}_2 \cdot [\text{CH}_2]_5 \cdot \text{CO}_2 \cdot \text{C}_{10}\text{H}_{19}$, is also an oil, boiling and decomposing at $248\text{--}252^\circ/20$ mm. At first it is almost colourless, but becomes converted into a brown, resinous substance on exposure to the air:

0.1357 gave 0.3688 CO_2 and 0.1361 H_2O . C = 74.11; H = 11.14.

$\text{C}_{27}\text{H}_{48}\text{O}_4$ requires C = 74.30; H = 11.01 per cent.

Dimenthyl Suberate, $\text{C}_{10}\text{H}_{19} \cdot \text{CO}_2 \cdot [\text{CH}_2]_6 \cdot \text{CO}_2 \cdot \text{C}_{10}\text{H}_{19}$.—A colourless oil, boiling at $257\text{--}259^\circ/20$ mm., and solidifying, after remaining for a long period in the cold, to a mass of crystals, which re-melt at $38\text{--}39^\circ$:

0.1076 gave 0.2934 CO_2 and 0.1046 H_2O . C = 74.35; H = 10.80.

$\text{C}_{28}\text{H}_{50}\text{O}_4$ requires C = 74.66; H = 11.11 per cent.

Dimenthyl Azelate, $\text{C}_{10}\text{H}_{19} \cdot \text{CO}_2 \cdot [\text{CH}_2]_7 \cdot \text{CO}_2 \cdot \text{C}_{10}\text{H}_{19}$.—A very viscous oil, boiling at $254\text{--}256^\circ/20$ mm., and remaining liquid after being cooled to -15° for some time:

0.1712 gave 0.4684 CO_2 and 0.1676 H_2O . C = 74.61; H = 10.88.

$\text{C}_{29}\text{H}_{52}\text{O}_4$ requires C = 75.01; H = 11.20 per cent.

Dimenthyl Sebacate, $C_{10}H_{19} \cdot CO_2 \cdot [CH_2]_8 \cdot CO_2 \cdot C_{10}H_{19}$.—This ester is a viscous liquid, which boils at $256-258^\circ/20$ mm., and resists all attempts to solidify it by cooling to -10° :

0.1122 gave 0.3100 CO_2 and 0.1110 H_2O . $C = 75.36$; $H = 10.99$.

$C_{30}H_{54}O_4$ requires $C = 75.32$; $H = 11.30$ per cent.

The *brucine* salts were, as in the previous work, made up directly from the constituents in chloroform solution, and then recovered for characterisation and analysis.

Dibrucine Oxalate, $C_2H_2O_4, C_{46}H_{52}O_8N_4, 4\frac{1}{2}H_2O$.—Small, white, cubical crystals, not very soluble in cold water, melting and losing water at 140° , then re-solidifying, and finally melting at 202° :

0.0985 gave 0.2161 CO_2 and 0.0618 H_2O . $C = 59.84$; $H = 6.97$.

$C_{48}H_{54}O_{12}N_4, 4\frac{1}{2}H_2O$ requires $C = 60.06$; $H = 6.63$ per cent.

Dibrucine Malonate, $C_3H_4O_4, C_{46}H_{52}O_8N_4, 3H_2O$.—Small, hard crystals, freely soluble in water, melting and losing water at 102° :

0.1788 gave 0.4086 CO_2 and 0.1062 H_2O . $C = 62.32$; $H = 6.75$.

$C_{49}H_{56}O_{12}N_4, 3H_2O$ requires $C = 62.16$; $H = 6.55$ per cent.

Dibrucine Glutarate, $C_5H_8O_4, C_{46}H_{52}O_8N_4, 4H_2O$.—A white, micro-crystalline powder, readily soluble in water, melting and decomposing at 114° :

0.1468 gave 0.3314 CO_2 and 0.0962 H_2O . $C = 61.56$; $H = 7.28$.

$C_{51}H_{60}O_{12}N_4, 4H_2O$ requires $C = 61.70$; $H = 6.86$ per cent.

Dibrucine Pimelate, $C_7H_{12}O_4, C_{46}H_{52}O_8N_4, 4H_2O$.—Very deliquescent crystals, melting and evolving water of crystallisation at 104° :

0.1240 gave 0.2822 CO_2 and 0.0804 H_2O . $C = 62.09$; $H = 7.20$.

$C_{53}H_{64}O_{12}N_4, 4H_2O$ requires $C = 62.36$; $H = 7.06$ per cent.

Dibrucine Suberate, $C_8H_{14}O_4, C_{46}H_{52}O_8N_4, 4\frac{1}{2}H_2O$.—Crisp, cream-coloured crystals, melting sharply at 102° to a clear liquid:

0.1356 gave 0.3082 CO_2 and 0.0872 H_2O . $C = 61.98$; $H = 7.15$.

$C_{54}H_{66}O_{12}N_4, 4\frac{1}{2}H_2O$ requires $C = 62.15$; $H = 7.19$ per cent.

Dibrucine Azelate, $C_9H_{16}O_4, C_{46}H_{52}O_8N_4, 3H_2O$.—Large, white, fibrous prisms, soluble in water, and melting at 96° :

0.1116 gave 0.2616 CO_2 and 0.0728 H_2O . $C = 63.92$; $H = 7.25$.

$C_{55}H_{68}O_{12}N_4, 3H_2O$ requires $C = 64.07$; $H = 7.19$ per cent.

Dibrucine Sebacate, $C_{10}H_{18}O_4, C_{46}H_{52}O_8N_4$.—Small, white, crystalline flakes from concentrated aqueous solutions, melting at 112° :

0.1296 gave 0.3234 CO_2 and 0.0870 H_2O . $C = 68.03$; $H = 7.46$.

$C_{56}H_{70}O_{12}N_4$ requires $C = 67.89$; $H = 7.07$ per cent.

The results of the polarimetric measurements (carried out as usual in dry chloroform solution at 15°) are collected in the following tables:

I. *Menthyl Esters.*

	Percentage concentration.					
	5.			2½.		
	[α] _D .	[M] _D .	Diff.	[α] _D .	[M] _D .	Diff.
Dimenthyl oxalate ...	-104.00°	-330.6°	57.7°	-103.40°	-378.4°	56.0°
„ malonate...	79.24	301.1	-19.8	79.54	302.6	-19.8
„ succinate...	81.90	322.7	1.8	82.40	324.6	2.2
„ glutarate...	80.26	328.3	7.4	80.16	327.1	4.7
„ adipate ...	83.80	353.6	32.7	83.60	352.8	30.4
„ pimelate ...	78.31	341.5	20.6	77.82	339.3	16.9
„ suberate ...	73.56	331.1	10.2	73.23	329.8	7.4
„ azelate.....	72.68	337.2	16.3	72.32	335.5	13.1
„ sebacate ...	67.08	320.6	-0.3	66.72	318.8	-3.6

II. *Brucine Salts.*

Dibrucine oxalate ..	-3.00°	-26.3°	472.8°	-2.80°	-24.6°	482.8°
„ malonate.	52.76	470.6	28.5	52.76	470.6	36.8
„ succinate.	65.30	591.6	-72.5	64.12	580.9	-73.5
„ glutarate.	50.62	465.8	33.3	50.48	464.4	43.0
„ adipate ...	42.80	399.2	99.9	42.60	397.8	109.6
„ pimelate ..	42.74	405.2	93.9	44.08	417.9	89.5
„ suberate..	45.70	439.6	59.5	47.56	457.5	49.9
„ azelate ...	45.16	440.8	58.3	45.52	444.2	63.2
„ sebacate ..	48.24	477.5	21.6	48.44	479.5	27.9

There are several points to which attention may be drawn with respect to these results. In the first place, the two series of results are approximately parallel, and this must be taken to signify that the changes produced in the activity of the asymmetric atoms in the compounds are due to the constitution of the acid part of the molecule.

Again, oxalic acid exhibits by far the greatest anomaly in both series, as might be expected from the contiguity in its molecule of two carboxyl groups rich in residual affinity. But if the anomalies of brucine and menthyl oxalates be compared with those occurring in the case of acids containing a conjugated ethenoid system (see previous paper), it will be found that, with the exception of muconic acid, none of these compounds exhibit such a marked effect as oxalic acid, although the "unsaturation" in the latter compound might be expected to be far weaker than that of two adjacent ethylenic groups. It seems likely, however, that, as with muconic acid and other compounds (*loc. cit.*), the symmetrical disposition of the molecule about the centre of the conjugated system is in some way the cause of the enhanced optical activity.

For the rest, from analogy to the normal fatty monobasic acids, one would have expected on first thoughts to see the molecular rotatory powers decreasing, rapidly at first, to an ultimately fairly constant

value, but, as a matter of fact, the series found are very far from regular.

There is, first of all, a pronounced depression between the first and fourth member of the series, while the fifth (adipic acid) presents a second maximum point on the graph. After this point the molecular rotatory powers seem to become more regular, and may possibly show to a small extent an alternation similar to that noticeable in the melting points of the free acids, but no definite information can be given regarding the ultimate shape of the anomaly curve, since a sufficient number of the higher members of the series has not been examined.

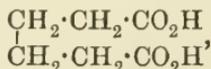
The two most noteworthy points are thus the depression in the second and third, and the exaltation in the fifth members of the series. With reference to the former, it is difficult to conceive of any explanation based on the constitution of the acids. It can only be said that the rotatory powers of dimethyl malonate and of dibrucine succinate are markedly lower than the normal value, and that a similar effect is to be seen in Walden's figures for di-*l*-amyl malonate (*loc. cit.*). Indeed, it would appear from the fragmentary evidence available that the amyl ester curve for these acids closely resembles that for the menthyl esters. It may be mentioned here that an exceptionally large temperature-coefficient was observed in the case of dibrucine succinate.

The exaltation in the adipic compounds admits, on the other hand, of a possible simple explanation. It finds a parallel in the simple fatty acid series, in which Rupe (*Annalen*, 1903, 327, 166) pointed out that an ethylenic or phenyl group in the δ -position with respect to the carboxyl group sometimes exercises a weakening effect on the rotatory power. It is obvious that the direction of the effect is not the same in both cases, but evidently optical activity is influenced by two unsaturated groups separated by a chain of four carbon atoms.

The exceptional chemical activity of different groups in this position is well known, and may be recalled by the ease with which water is eliminated from many dihydroxylic compounds of this type, yielding lactones or anhydrides:



The same steric hypothesis which presupposes the contiguity in space of the hydroxyl groups in such cases would necessitate the carboxyl groups as a whole being close to each other in adipic acid,



and it may therefore be that the same influence which causes the

large anomaly in oxalic acid derivatives causes the enhanced rotatory power here, namely, the conjunction of two unsaturated groups. The effect is not unnaturally much less than that observed when the two conjugated systems are chemically united, and this would account for its non-appearance in other physical properties less susceptible to constitutive changes than optical activity.

In conclusion, the author wishes to express his great indebtedness to Assistant Prof. Smiles for criticising the work described in this and the preceding paper, the cost of which has been partly met by a grant from the Research Fund of the Chemical Society.

UNIVERSITY OF JENA.

CLXXIX.—*Some Derivatives of l-Benzoin.*

By HENRY WREN.

THE preparation of *l*-benzoin by the action of magnesium phenyl bromide on *l*-mandelamide has already been described (McKenzie and Wren, *Trans.*, 1908, **93**, 310). Since this compound is the first example of an optically active ketol of simple structure, it was considered of interest to make a further study of it and some of its derivatives, and also to prepare its enantiomorphous isomeride. The work carried out in this direction is described in this and the following paper.

EXPERIMENTAL.

Preparation of d-Benzoin.

Methyl *d*-mandelate (25 grams) was converted into *d*-mandelamide, $C_6H_5 \cdot CH(OH) \cdot CO \cdot NH_2$, by the method previously described (*loc. cit.*) for the preparation of *l*-mandelamide from methyl *l*-mandelate. The yield amounted to 13 grams :

0.1756 gave 0.4096 CO_2 and 0.0928 H_2O . C = 63.6 ; H = 5.9.

0.1886 „ 14.9 c.c. N_2 at 12° and 771 mm. N = 9.6.

$C_8H_9O_2N$ requires C = 63.6 ; H = 6.0 ; N = 9.3 per cent.

This amide resembles its enantiomorphous isomeride in appearance, melting point (122 — 122.5°), solubility, and specific rotation. The latter was determined in acetone solution :

$l = 4$, $c = 1.6496$, $\alpha_D^{20} + 4.93^\circ$, $[\alpha]_D^{20} + 74.7^\circ$.

The value previously found for *l*-mandelamide under similar conditions was -73.1° .

d-Benzoin, $C_6H_5 \cdot CH(OH) \cdot CO \cdot C_6H_5$, obtained from *d*-mandelamide and magnesium phenyl bromide, crystallises from methyl alcohol in colourless needles, and has the same melting point as *l*-benzoin (131—132·5°):

0·1156 gave 0·3342 CO_2 and 0·0588 H_2O . C = 78·8; H = 5·7.

$C_{14}H_{12}O_2$ requires C = 79·2; H = 5·7 per cent.

Its specific rotation was determined in acetone solution:

$l = 4$, $c = 0\cdot4128$, $\alpha_D^{11\cdot5} + 1\cdot99^\circ$, $[\alpha]_D^{11\cdot5} + 120\cdot5^\circ$.

l-Benzoin dissolved in acetone has $[\alpha]_D^{10\cdot5} - 118\cdot6^\circ$ for $c = 0\cdot9232$.

d-Benzoin was converted into benzil (m. p. 95—96°) by the action of concentrated nitric acid.

Methylation of l-Benzoin.

For the methylation of *l*-benzoin, Purdie's silver oxide method of alkylation was employed (compare Lander, *Trans.*, 1900, **77**, 734; Irvine and Weir, *Trans.*, 1907, **91**, 1391), as being less likely than any of the other methods to give a partly racemised product. It was also used in preference to the hydrochloric acid method by means of which *r*-benzoin was methylated (Fischer, *Ber.*, 1893, **26**, 2412), since it has been shown (Irvine and Weir, *loc. cit.*; Irvine and McNicoll, *Trans.*, 1908, **93**, 952) that in the latter reaction the formation of *r*-benzoin methyl ether is accompanied by that of $\alpha\beta$ -dibenzoyl- α -methoxydibenzyl and 2-hydroxy-3:5-dimethoxytetraphenyltetrahydrofuran.

Dry silver oxide (21 grams, 2·7 mols.) was added to a solution of *l*-benzoin (7·3 grams, 1 mol.) and methyl iodide (43·9 grams, 9 mols.) in acetone (100 c.c.). On warming, gentle boiling set in, which lasted about ten minutes. The mixture was subsequently boiled gently with frequent shaking during two hours, after which time the precipitate of silver oxide and silver iodide was filtered and well washed with acetone. The residue, obtained after removal of the acetone, solidified readily to a mass of yellow crystals weighing 6·9 grams.

The crude *l*-benzoin methyl ether was purified by being crystallised from light petroleum until the value of its specific rotation in chloroform solution was constant.

l-Benzoin methyl ether, $C_6H_5 \cdot CH(OMe) \cdot CO \cdot C_6H_5$, separates from boiling light petroleum in well-defined, rectangular prisms, melting at 53—54°:

0·1272 gave 0·3717 CO_2 and 0·0713 H_2O . C = 79·69; H = 6·27.

$C_{15}H_{14}O_2$ requires C = 79·62; H = 6·24 per cent.

It is readily soluble in the ordinary organic solvents with the exception of cold light petroleum, in which it is very sparingly soluble.

Its specific rotation in chloroform solution was as follows:

$$l = 4, c = 2.1108, \alpha_D^{12} - 7.45^\circ, [\alpha]_D^{12} - 88.2^\circ.$$

Its specific rotation was also determined in solution in heptane, benzene, and ethyl alcohol respectively. In heptane solution:

$$l = 4, c = 0.5648, \alpha_D^{15} + 3.34^\circ, [\alpha]_D^{15} + 147.8^\circ.$$

The heptane was optically inactive. It was obtained by fractionating Kahlbaum's heptane, and boiled at 97—98°. In ethyl-alcoholic solution:

$$l = 4, c = 0.5860, \alpha_D^{11} - 2.21^\circ, [\alpha]_D^{11} - 94.3^\circ.$$

In benzene solution:

$$l = 4, c = 0.6428, \alpha_D^{15} + 1.31^\circ, [\alpha]_D^{15} + 50.9^\circ.$$

The *l*-benzoin methyl ether was recovered unchanged from each of the above solutions.

It is thus apparent that *l*-benzoin methyl ether is strongly dextrorotatory when dissolved in heptane or benzene, whilst it is strongly levorotatory in chloroform or ethyl-alcoholic solution. Similar alteration in the sign of rotation with variation of solvent has been observed with a few non-ionised substances. Thus, dimethyl *d*-tartrate is dextrorotatory when dissolved in acetone, methyl alcohol, or acetonitrile, levorotatory when dissolved in benzene or chloroform, whilst in ethyl acetate the sign of rotation varies with the temperature (Walden, *Ber.*, 1905, 38, 385). Similarly, dimethyl *l*-malate is levorotatory when dissolved in acetone, methyl alcohol, or ethyl acetate, but dextrorotatory in chloroform. In benzene solution the sign of rotation depends on the temperature and concentration (Walden, *loc. cit.*). Similar observations have been made by Freundler (*Compt. rend.*, 1893, 117, 556; *Ann. Chim. Phys.*, 1895, [vii], 4, 244) in the cases of the normal propyl esters of diacetyl-*d*-tartaric acid, dibutyryl-*d*-tartaric acid, and dihexoyl-*d*-tartaric acid, but in no case are the variations so marked as in that of *l*-benzoin methyl ether.

Acetyl-l-benzoin.

l-Benzoin (1.6 grams) was warmed with acetyl chloride (3 grams). Solution of the benzoin was complete at 35°. The temperature of the mixture was maintained at 40—50° during one hour, after which it was gradually raised to 100° and maintained at this point until evolution of hydrogen chloride ceased. Excess of acetyl chloride was removed by allowing the product to remain under diminished pressure over soda-lime.

Acetyl-l-benzoin, $C_6H_5 \cdot CH(O \cdot CO \cdot CH_3) \cdot CO \cdot C_6H_5$, separates from boiling light petroleum in colourless needles, sometimes grouped in rosettes. It is readily soluble in hot light petroleum, and in cold

ether, methyl and ethyl alcohols, acetone, chloroform, benzene, or glacial acetic acid. In cold light petroleum it is sparingly soluble:

0.1204 gave 0.3316 CO_2 and 0.0612 H_2O . $\text{C} = 75.1$; $\text{H} = 5.7$.

$\text{C}_{16}\text{H}_{14}\text{O}_3$ requires $\text{C} = 75.5$; $\text{H} = 5.6$ per cent.

The specific rotation of successive crops from light petroleum was determined in chloroform solution:

$l = 4$, $c = 1.0116$, $\alpha_D^{14} = 8.81^\circ$, $[\alpha]_D^{14} = 217.7^\circ$.

$l = 4$, $c = 0.7240$, $\alpha_D^{14.5} = 6.31^\circ$, $[\alpha]_D^{14.5} = 217.9^\circ$.

Carbanilido-l-benzoin.

A mixture of *l*-benzoin (2 grams) and phenylcarbimide (3 grams) was heated on the boiling-water bath during thirty minutes. The benzoin rapidly dissolved to a somewhat brown solution, which partly solidified on cooling. The excess of phenylcarbimide was removed by means of light petroleum, and the solid residue, consisting of carbanilido-*l*-benzoin together with small quantities of carbanilido-*r*-benzoin and diphenylcarbamide, was triturated with a small quantity of cold ethyl acetate, in which diphenylcarbamide is insoluble. After filtration and removal of ethyl acetate from the filtrate, the crude carbanilido-*l*-benzoin was purified by recrystallisation from methyl alcohol, and finally from light petroleum (b. p. 60—80°).

Carbanilido-l-benzoin, $\text{C}_6\text{H}_5 \cdot \text{CH}(\text{O} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_5) \cdot \text{CO} \cdot \text{C}_6\text{H}_5$, separates from boiling light petroleum, in which it is sparingly soluble, in rather ill-defined, colourless crystals. It dissolves readily in cold benzene, ethyl alcohol, acetone, ether, chloroform, ethyl acetate, or pyridine. It is moderately soluble in cold methyl alcohol, readily so in the boiling solvent. It melts at 121.5° to a clear liquid, which, when heated through a further 2° or 3°, again solidifies, re-melting at 163.5°. The latter temperature agrees with the melting point (163°) given by Gumpert (*J. pr. Chem.*, 1885, [ii], 32, 280) for carbanilido-*r*-benzoin:

0.1499 gave 0.4201 CO_2 and 0.0726 H_2O . $\text{C} = 76.4$; $\text{H} = 5.4$.

$\text{C}_{21}\text{H}_{17}\text{O}_3\text{N}$ requires $\text{C} = 76.1$; $\text{H} = 5.2$ per cent.

For the determination of the specific rotation in benzene solution, successive crops from light petroleum were dried in a vacuum over paraffin wax until constant in weight:

$l = 4$, $c = 0.8228$, $\alpha_D^{15.7} = 9.57^\circ$, $[\alpha]_D^{15.7} = 290.8^\circ$.

$l = 4$, $c = 0.8024$, $\alpha_D^{18} = 9.37^\circ$, $[\alpha]_D^{18} = 291.9^\circ$.

The specific rotation was also determined in acetone solution:

$l = 4$, $c = 0.6528$, $\alpha_D^{21} = 5.61^\circ$, $[\alpha]_D^{21} = 214.8^\circ$.

Interaction of l-Benzoin and Hydroxylamine.

The study of the interaction of hydroxylamine and *l*-benzoin was of particular interest, owing to the mutarotation of the α -oxime which was observed in various solvents.

l-Benzoin- α -oxime.

A mixture of *l*-benzoin (5.6 grams) and ethyl alcohol (22.4 c.c.), to which had been added solutions of hydroxylamine hydrochloride (4.5 grams in 5.6 c.c. water) and sodium hydroxide (2.5 grams in 6.8 c.c. water), was heated for one hour on the boiling-water bath, and, after cooling, poured into water (200 c.c.). A bulky, white precipitate (5.1 grams) separated, from which, after two recrystallisations from benzene, *l*-benzoin- α -oxime (2 grams) was obtained as a white, amorphous powder, which melted at 163.5—164.5°:

0.1273 gave 0.3432 CO₂ and 0.0661 H₂O. C = 73.5; H = 5.8.

0.1327 „ 7.2 c.c. N₂ at 15° and 751 mm. N = 6.4.

C₁₄H₁₃O₂N requires C = 74.0; H = 5.8; N = 6.2 per cent.

l-Benzoin- α -oxime is moderately soluble in boiling benzene, very sparingly in the cold solvent. Its specific rotation was determined in a number of solvents.

In chloroform solution:

$$l = 4, c = 0.8576, \alpha_D^{24} - 0.11^\circ, [\alpha]_D^{24} - 3.2^\circ.$$

This value did not change during twenty-one hours. After removal of the solvent at the ordinary temperature, the residue melted at 163.5—164°.

In ethyl-alcoholic solution:

$$l = 4, c = 0.9648, \alpha_D^{23} + 0.17^\circ, [\alpha]_D^{23} + 4.4^\circ.$$

During twenty-two hours the activity of the solution remained constant. The residue, after removal of alcohol, melted at 163—163.5°.

In ethyl benzoate solution:

$$l = 4, c = 0.4724, \alpha_D^{23.3} + 0.70^\circ, [\alpha]_D^{23.3} + 37.0^\circ.$$

This solution showed no change in activity during nineteen hours.

In acetone solution:

$$\text{Expt. I.}—l = 4, c = 0.7068, \alpha_D^{15} + 0.51^\circ, [\alpha]_D^{15} + 18.0^\circ.$$

The polarimetric determination was performed immediately after the solution was made up. The solution was allowed to evaporate in an open dish at the ordinary temperature. The residue, after being dried in a vacuum, melted at 162.5°.

$$\text{Expt. II.}—l = 4, c = 1.6892.$$

In this experiment mutarotation was observed.

Time in hours.	$\alpha_D^{15^\circ}$.	$[\alpha]_D^{15^\circ}$.	Time in hours.	$\alpha_D^{15^\circ}$.	$[\alpha]_D^{15^\circ}$.
2.25	+2.15°	+31.8°	22.8	+10.22°	+151.2°
3.25	3.31	49.0	27.5	9.97	147.5
5.33	6.43	95.1	29.8	9.87	146.1
7.33	8.36	123.7	47.0	9.56	141.5
8.33	8.92	132.0	56.3	9.50	140.6
9.33	9.35	138.3	95.0	9.37	138.6
10.33	9.72	143.8			

On evaporation, the solution left a viscous residue.

Expt. III.— $l = 4$, $c = 0.9803$, $t = 23.7 \pm 0.2^\circ$.

Time in hours.	α_D .	$[\alpha]_D$.	Time in hours.	α_D .	$[\alpha]_D$.
0.75	+0.92°	+23.5°	4.75	+5.17°	+131.8°
1.25	1.71	43.6	5.75	5.37	136.9
1.75	2.16	55.1	6.75	5.47	139.4
2.25	4.12	105.0	7.75	5.48	139.7
2.75	4.45	113.4	8.75	5.44	138.6
3.25	4.69	119.5	23.25	5.42	138.1
3.75	4.84	123.4			

Expt. IV.—Solvent: Acetone to which one drop of piperidine per 5 c.c. solvent had been added:

$$l = 4, c = 1.034, \alpha_D^{23.2} + 0.75^\circ, [\alpha]_D^{23.2} + 18.1^\circ.$$

The activity of this solution remained constant during twenty hours. After removal of the solvent, the residue melted at 150—159°.

The α -oxime exhibited mutarotation in acetophenone solution:

$$l = 4, c = 0.8928, t = 23.5 \pm 0.3^\circ.$$

Time in hours.	α_D .	$[\alpha]_D$.	Time in hours.	α_D .	$[\alpha]_D$.
0.5	+1.84°	+51.5°	5.75	+2.70°	+75.6°
0.75	1.79	50.1	6.75	2.83	79.2
1.25	1.79	50.1	7.5	2.87	80.3
2.75	1.98	55.4	25.0	3.61	101.1
3.75	2.28	63.5	25.5	3.64	101.9
4.75	2.45	68.6			

In benzaldehyde solution:

$$l = 4, c = 0.8552, t = 23.8 \pm 0.1^\circ.$$

Time in hours.	α_D .	$[\alpha]_D$.	Time in hours.	α_D .	$[\alpha]_D$.
0.25	+0.91°	+26.6°	4.25	+0.99°	+28.9°
1.25	0.91	26.6	5.25	1.06	30.9
2.25	0.96	28.1	23.5 ($t = 18^\circ$)	1.61	47.1
3.25	0.98	28.6			

In methyl ethyl ketone solution:

$$l = 4, c = 2.1364, \alpha_D^{23.8} + 2.11^\circ, [\alpha]_D^{23.8} + 24.7^\circ.$$

The value of α_D remained absolutely constant during three and a-quarter hours. After forty-six hours it had only increased to 2.28°. The residue, after removal of the solvent, melted rather indefinitely at 153—158°.

Mutarotation of *l*-benzoin- α -oxime was thus observed in acetone, acetophenone, benzaldehyde, and methyl ethyl ketone solution, whilst no mutarotation was observed with chloroform, ethyl alcohol, and ethyl benzoate. In this connexion it is interesting to note that Lowry (Trans., 1899, 75, 219) has shown that the equilibrium between nitrocamphor and ψ -nitrocamphor is attained far more rapidly in acetone than in any other solvent, under similar conditions of temperature and concentration. It therefore seems possible that mutarotation in the case of non-ketonic or -aldehydic solvents was not observed, since the velocity of change in these media is extremely small. Even in aldehydic and ketonic solvents some external impulse appears to be necessary to start the change. Thus, in one case *l*-benzoin- α -oxime was recovered practically unchanged from acetone solution. Further, a solution of the substance in benzaldehyde was kept in the polarimeter tube for two and a-quarter hours before change commenced, whilst a solution in acetophenone showed no change during about two hours, at the end of which period reaction started and then proceeded in the usual manner.

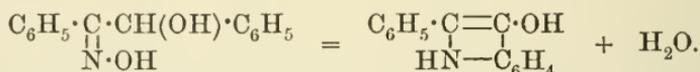
Lowry (Trans., 1899, 75, 221; 1903, 83, 317) and Lowry and Magson (Trans., 1908, 93, 107) have shown the striking effects of traces of various catalysts on solutions of *d*-glucose and nitrocamphor in different solvents. Some such catalytic influence seems also to come into play in the case of *l*-benzoin- α -oxime. Up to the present it has not been possible to identify the catalyst. The influence of piperidine on the change in acetone solution was investigated, and found to be inhibitive. It seems most probable that *l*-benzoin- α -oxime, when dissolved in ketonic or aldehydic solvents, gradually passes into the isomeric β -oxime. Unfortunately, no pure substance could be isolated from the viscous residues which were obtained on evaporating solutions in which mutarotation had taken place, nor could pure *l*-benzoin- β -oxime be isolated. Evidence has, however, been obtained to show that the latter is strongly dextrorotatory.

To test the relationship between *l*-benzoin- α -oxime and *l*-benzoin, the former was treated according to the method given by Lapworth (Trans., 1907, 91, 1133) for the decomposition of camphoroxime.

l-Benzoin- α -oxime (0.9 gram) was warmed with a solution of formaldehyde (20 c.c.) and concentrated hydrochloric acid (15 c.c.). The oxime rapidly passed into solution, from which a white precipitate soon began to separate. After warming for twenty-five minutes, the reaction mixture was poured into water. The precipitate which separated was identified as *l*-benzoin by its melting point and rotation. No Walden inversion was thus detected.

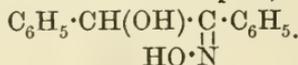
Interaction of l-Benzoin- α -oxime and Concentrated Sulphuric Acid.

The configuration of the α - and β -oximes of *r*-benzoin has been studied more particularly by Werner and Detscheff (*Ber.*, 1905, 38, 73), Werner and Piguet (*Ber.*, 1904, 37, 4295), and E. Fischer and Hütz (*Ber.*, 1895, 28, 585). The latter investigators showed that the α -oxime is converted in good yield into α -phenylindoxyl by the action of cold concentrated sulphuric acid. Since a rather impure specimen of *r*-benzoin- β -oxime under the same conditions gave only a small amount of α -phenylindoxyl, the formation of which was probably attributable to the *r*-benzoin- α -oxime present, it follows that the latter contains the $\cdot\text{OH}$ and $\cdot\text{CH}(\text{OH})\cdot\text{C}_6\text{H}_5$ groups in the *cis*-position. Its transformation into α -phenylindoxyl may then be represented by the equation:



Werner and Detscheff (*loc. cit.*) have shown that pure *r*-benzoin- β -oxime does not yield α -phenylindoxyl when acted on by sulphuric acid.

The action of concentrated sulphuric acid on *l*-benzoin- α -oxime was carried out in accordance with the directions given by Fischer and Hütz (*loc. cit.*). Yellow needles were obtained which showed all the reactions of α -phenylindoxyl. They melted at $170\cdot5$ — 171° , gas evolution and decomposition occurring at a slightly higher temperature. When mixed with an approximately equal quantity of α -phenylindoxyl, prepared from pure *r*-benzoin- α -oxime, the melting point was practically unchanged ($170\cdot5^\circ$) with the same phenomena as previously noticed. Fischer and Hütz quote "about 175° " as the melting point of α -phenylindoxyl. It follows then that, if the Hantzsch-Werner interpretation of the isomerism of oximes is accepted, the configuration of *l*-benzoin- α -oxime must be:

*Attempted Isolation of l-Benzoin- β -oxime.*

In the preparation of *l*-benzoin- α -oxime it was noticed that considerable loss occurred when the crude oxime was purified by recrystallisation from benzene. The benzene mother liquors were therefore evaporated to dryness in a vacuum, when a pasty mass, mixed with a few solid particles, remained, which did not solidify further when kept in a vacuum during several weeks. It was mixed with a small quantity of ether, and the solution so obtained filtered from the small quantity of undissolved *l*-benzoin- α -oxime. When the ethereal filtrate was

again evaporated in a vacuum, a pasty mass again resulted, which dissolved in practically all organic solvents, and could not be obtained from them in a crystalline state. By dissolving the mass in warm carbon tetrachloride and cautiously adding light petroleum, a small amount of solid was precipitated, which, after drying, melted indefinitely at 136—154°. Its specific rotation was determined in ethyl-alcoholic solution :

$$l = 2, c = 0.896, \alpha_D + 1.18^\circ, [\alpha]_D + 65.8^\circ.$$

l-Benzoin- α -oxime has $[\alpha]_D^{23} + 4.4^\circ$ in ethyl-alcoholic solution. Since Werner and Detscheff (*loc. cit.*) have shown that the production of racemic β -oxime always accompanies that of the racemic α -oxime, it appears valid to conclude that the above compound was crude *l*-benzoin- β -oxime. The amount of material was too small to allow further purification.

An attempt was then made to prepare *l*-benzoin- β -oxime directly, according to the directions given by Werner and Detscheff (*loc. cit.*) for the preparation of *r*-benzoin- β -oxime.

l-Benzoin (2 grams) was covered with a mixture of ethyl alcohol (8 grams) and water (12 grams). To this a solution of hydroxylamine hydrochloride (0.9 gram in 2 c.c. of water), mixed with 10.4 c.c. of 2.5*N*-sodium hydroxide solution, was added. The mixture was warmed in the water-bath at 50—60° with brisk shaking until, after eighteen minutes, all the benzoin had passed into solution. After cooling, the mixture was poured into water, and the oxime liberated by carbon dioxide and extracted with ether. After drying the ethereal solution and removing the ether, a pasty mass remained which did not solidify completely. It was redissolved in dry ether, and, on allowing the ethereal solution to evaporate gradually, two small crops of crystals were obtained, which melted at 151—152° and 149—150° respectively. When united and examined in acetone solution, they were found to be optically inactive, and therefore consisted of *r*-benzoin- α -oxime. The ethereal solution, from which the crops had been removed, was strongly dextrorotatory. The whole solution, examined in a 1-dm. tube, had $\alpha_D + 6.66^\circ$. Further efforts to obtain a solid oxime from it were fruitless, viscous products being invariably obtained which could not be caused to crystallise.

Interaction of l-Benzoin and Semicarbazide Hydrochloride.

Biltz (*Annalen*, 1905, 339, 257) has described the preparation of *r*-benzoinsemicarbazone by the interaction of an alcoholic suspension of *r*-benzoin and an aqueous solution of semicarbazide hydrochloride. An attempt was made to prepare *l*-benzoinsemicarbazone by the same method;

l-Benzoïn (2 grams) was dissolved in boiling ethyl alcohol (47 c.c.) and the solution rapidly cooled to the ordinary temperature, whereupon a portion of the benzoïn separated. After the addition of a solution of semicarbazide hydrochloride (1 gram) in water (3 c.c.), the mixture was shaken in a thermostat at 25° during five days. The clear yellow solution so formed was evaporated to dryness in a vacuum, and the residue washed with water and recrystallised from aqueous alcohol. The crystals so obtained melted at 129—131°, and proved to be slightly racemised *l*-benzoïn :

0.1284 gave 0.3716 CO₂ and 0.0667 H₂O. C = 78.9; H = 5.8.

C₁₄H₁₂O₂ requires C = 79.2; H = 5.7 per cent.

l = 2, *c* = 1.1295, α_D - 2.39°, $[\alpha]_D$ - 105.8°.

Preparation of Phenylacetylcarbinol.

It was hoped that a series of optically active ketols, of the general formula C₆H₅·CH(OH)·CO·R, might be obtained by the action of Grignard's reagent on *l*-mandelamide. As a preliminary experiment, the reaction of *r*-mandelamide with magnesium methyl iodide was investigated, when phenylacetylcarbinol was obtained in small yield. This ketol is a liquid. Assuming that the active isomeride is also a liquid, it would be difficult to prove that it contained none of the inactive variety, if prepared by this method. This line of work was therefore abandoned for the present.

r-Mandelamide (20 grams) was gradually added, within an interval of twenty-five minutes, to a well-cooled solution of the Grignard reagent prepared from magnesium (18.8 grams), methyl iodide (111.2 grams), and ether (250 c.c.). When all the amide had been added, the reaction mixture was gently boiled during eight and a-half hours, after which it was decomposed by ice and sulphuric acid in the usual manner. The liberated phenylacetylcarbinol was extracted with ether and obtained as a pale yellow oil (3.5 grams), which boiled at 138—140°/23 mm. :

0.1578 gave 0.4140 CO₂ and 0.0966 H₂O. C = 71.6; H = 6.8.

C₉H₁₀O₂ requires C = 72.0; H = 6.7 per cent.

Phenylacetylcarbinol, C₆H₅·CH(OH)·CO·CH₃, unlike methylacetylcarbinol described by Diels and Stephan (*Ber.*, 1907, 40, 4338), does not solidify when placed in a freezing mixture, when preserved during several months, or when brought into contact with metallic zinc. It is insoluble in water, but readily miscible with organic solvents. It reduces Fehling's solution, alkaline permanganate, and ammoniacal silver solution in the cold. In alcoholic aqueous solution it gives no coloration with ferric chloride.

Carapelle (*Gazzetta*, 1903, 33, [ii], 263) has prepared the same sub-

stance from benzyl methyl ketone. He gives the boiling point as $135^{\circ}/40$ mm.

Phenylacetylcarbinolsemicarbazone separates from boiling toluene as a white, amorphous powder, and melts at 194° . It is sparingly soluble in boiling toluene, benzene, ether, chloroform, or acetone, moderately so in boiling methyl or ethyl alcohol, and readily so in boiling glacial acetic acid :

0.1589 gave 0.3360 CO_2 and 0.0905 H_2O . C = 57.7; H = 6.4.

0.1508 ,, 26.3 c.c. N_2 at 18° and 760 mm. N = 20.5.

$\text{C}_{10}\text{H}_{13}\text{O}_2\text{N}_3$ requires C = 58.0; H = 6.3; N = 20.3 per cent.

The author desires to express his indebtedness to the Research Fund Committee of the Chemical Society for a grant, which has defrayed a portion of the expense of this research.

BIRKBECK COLLEGE,
LONDON, E. C.

CLXXX.—*Racemisation Phenomena observed in the Study of l-Benzoin and its Derivatives.*

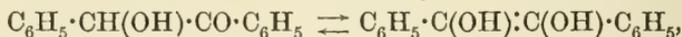
By HENRY WREN.

IN a recent paper entitled "Studien über katalytische Razemisierung," Winther (*Zeitsch. physikal. Chem.*, 1906, **56**, 465) has divided the known cases of racemisation—which is defined as the transformation of an optically active substance into an *isomeric* inactive substance—into four classes: (1) autoracemisation, (2) racemisation by heat, (3) racemisation due to the catalytic action of water or bases, and (4) racemisation due to other catalysts, for instance, hydrochloric acid, sulphuric acid, and aluminium chloride. In close connexion with this phenomenon are those cases in which optical activity is wholly or partly lost during the conversion of an optically active substance into one of its derivatives.

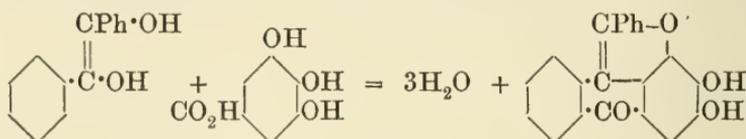
During a study of the derivatives of *l*-benzoin, frequent instances of racemisation have been encountered. *l*-Benzoin ethyl ether is partly, and carbanilido-*l*-benzoin completely, racemised under the action of heat. *l*-Benzoin and its methyl ether are completely and rapidly racemised by the action of alcoholic potash or sodium ethoxide. Further, methyl *l*-mandelate undergoes partial racemisation during conversion into *l*-mandelamide by the action of cold ethyl-alcoholic ammonia, whilst under the action of benzoyl chloride at a rather high temperature, of aniline at 100° , and of a saturated solution of hydrogen chloride in

ethyl alcohol at a temperature not exceeding 40°, *l*-benzoin is converted into derivatives of inactive benzoin. Lastly, *l*-benzoin- α -oxime undergoes partial racemisation when acetylated by means of acetic anhydride.

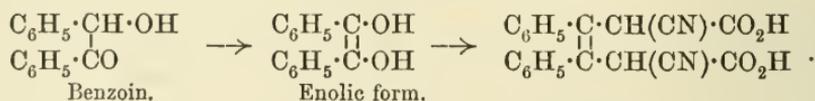
The racemisation of *l*-benzoin and of its methyl ether by alkali is of special interest, since it is probably attributable to keto-enolic change. Such a possibility in the case of *r*-benzoin has been indicated by several investigators. Thus Graebe (*Ber.*, 1898, 31, 2975) showed that benzoin, under the influence of sulphuric acid, condenses with gallic acid to form benzoin-yellow. The assumption is made that benzoin is first converted into ω -dihydroxystilbene, thus :



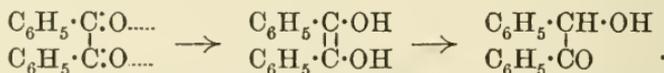
which then reacts in accordance with the equation :



Similarly, Haworth (*Trans.*, 1909, 95, 486) has shown that benzoin condenses with the sodium derivative of ethyl cyanoacetate, forming $\alpha\delta$ -dicyano- $\beta\gamma$ -diphenyl- Δ^{β} -butene- $\alpha\delta$ -dicarboxylic acid, a reaction which is explicable on the assumption that benzoin is first converted into ω -dihydroxystilbene, and that this substance then condenses with the sodiocyano-ester according to the following scheme :



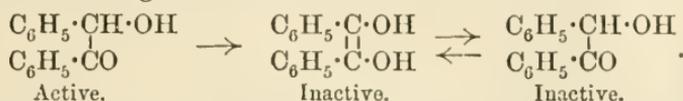
The reverse transformation, that of ω -dihydroxystilbene into benzoin, occurs, according to Thiele (*Annalen*, 1899, 306, 142), when benzil is reduced to benzoin, the course of the reaction being indicated by the scheme :



Although ω -dihydroxystilbene itself could not be isolated, derivatives of it were obtained by Thiele. Thus, when a solution of benzil in acetic anhydride, to which a little sulphuric acid had been added, was reduced by zinc dust, two stereoisomeric forms of ω -diacetoxystilbene were obtained, each of which yielded benzoin when hydrolysed with alcoholic potash. Similarly, Nef (*Annalen*, 1899, 308, 289) showed that the addition of acetic anhydride to the product of the action of sodium on a dry ethereal solution of benzil resulted in the formation of ω -diacetoxystilbene, a product identical with one of the modifications previously obtained by Thiele.

A similar transformation is to be expected with *l*-benzoin, the active

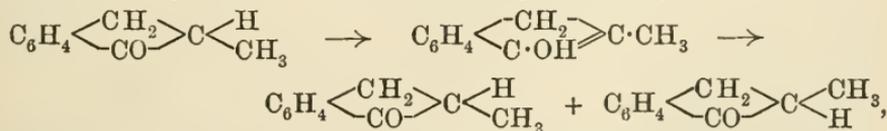
benzoin passing into inactive ω -dihydroxystilbene, from which inactive benzoin would be regenerated :



l-Benzoin might thus be expected to undergo autoracemisation. In ordinary circumstances, however, the velocity of transformation of *l*-benzoin into ω -dihydroxystilbene is so slow that the substance behaves as a stable active compound. Thus a solution of *l*-benzoin in acetone was found to retain its activity unchanged during eight days, whilst a crystalline specimen showed no change in activity during three months.

The presence of a trace of alkali has been repeatedly shown to favour the enolic form in the case of keto-enolic desmotropy. In the case of *l*-benzoin, the presence of potassium hydroxide or of a trace of sodium ethoxide so increases the velocity of the reaction *l*-benzoin \rightarrow ω -dihydroxystilbene that, in the course of a few hours, the active benzoin is completely converted into the inactive form. In neither of the above cases was direct polarimetric observation possible, since the addition of alkali causes alcoholic solutions of benzoin to acquire a purple coloration. This disadvantage is not encountered when *l*-benzoin methyl ether is used. It could then be shown that a solution of the latter in cold alcoholic potash (0.113*N*) became completely inactive within five minutes, whilst, under the action of sodium ethoxide, an alcoholic solution of the same substance showed no activity after three and a-half hours.

In a few cases, racemisation has previously been attributed to keto-enolic change. Kipping (Proc., 1902, 18, 34; compare Salway and Kipping, this vol., 167) ascribes the ready racemisation of *d*- β -methylhydrindone by alkali to isodynamic change according to the scheme :



whilst the transformation of *d*-camphoric acid into *l*-isocamphoric acid when heated with water is probably also due to the same cause (compare Lowry, *Brit. Assoc. Report*, 1904, 211).

EXPERIMENTAL.

Interaction of Methyl l-Mandelate and Alcoholic Ammonia.

The conversion of methyl *l*-mandelate into *l*-mandelamide has been described by McKenzie and Wren (Trans., 1908, 93, 312). A more extended study of this reaction has shown that this change is apt to

be accompanied by a certain amount of racemisation. In order to obtain the maximum yield of *l*-mandelamide, the experimental conditions have been slightly altered. The following experiment may be considered as typical:

A solution of methyl *l*-mandelate (74 grams, $[\alpha]_D - 236^\circ$ for $c = 3.6335$ in carbon disulphide solution*) in ethyl alcohol (74 c.c.) was cooled in ice and treated with a brisk current of dry ammonia during thirty minutes. Subsequently, the ice was replaced by a freezing mixture of ice and salt, and the passage of ammonia continued for a further period of forty-five minutes. The flask was tightly corked, when, after a few hours, a copious precipitate of *l*-mandelamide separated. The next day the mixture was cooled in a freezing mixture and the precipitate collected, ground with ether, and again filtered. The yield of *l*-mandelamide was 44 grams. Its specific rotation was determined in acetone solution:

$$l = 2, c = 1.685, \alpha_D - 2.42^\circ, [\alpha]_D - 71.8^\circ.$$

The pure amide (*loc. cit.*), dissolved in acetone, has $[\alpha]_D - 73.1^\circ$ ($c = 1.6416$).

The alcoholic-ammoniacal filtrate obtained above was evaporated in a vacuum at the ordinary temperature. The semi-solid mass which remained was triturated with ether and filtered, whereby a further crop (4.5 grams) was isolated, which, when dissolved in acetone, had $[\alpha]_D - 62.4^\circ$, and thus contained some of the *r*-amide:

$$l = 2, c = 2.235, \alpha_D - 2.79^\circ, [\alpha]_D - 62.4^\circ.$$

The conversion of the ester into amide is never complete. The unattacked ester was recovered by washing the ethereal solutions, obtained during the purification of the crude amide, successively with water, dilute sulphuric acid, and finally with water. After drying the solution over anhydrous sodium sulphate and removal of ether, the residue was distilled under diminished pressure. The ester so recovered from different experiments possessed specific rotations varying between -198° and -227° when dissolved in carbon disulphide.

l-Mandelamide itself does not appear to suffer racemisation when its solution in cold alcoholic ammonia is allowed to remain at the ordinary temperature for some time. Thus a partly racemised specimen of the amide, which possessed $[\alpha]_D - 62.8^\circ$ in acetone solution, was dissolved in alcohol and the solution saturated with ammonia. The solution was kept for six days at 10° , after which the alcohol and ammonia were removed under diminished pressure at the ordinary

* Walden (*Zeitsch. physikal. Chem.*, 1895, 17, 706) gives the values $[\alpha]_D - 214.1^\circ$ for $c = 3.33$ and $[\alpha]_D - 217.0^\circ$ for $c = 1.67$ for the specific rotation of methyl *l*-mandelate in carbon disulphide. The examination of several specimens of the ester has shown that this value is rather low.

temperature. The residual amide had $[\alpha]_D - 62.3^\circ$ in acetone solution :

$$l = 2, c = 3.306, \alpha_D - 4.12^\circ, [\alpha]_D - 62.3^\circ.$$

Partly racemised *l*-mandelamide cannot be economically purified by recrystallisation if its specific rotation falls below about -65° . In one case, a sample of amide (7 grams), possessing $[\alpha]_D - 60^\circ$ in acetone solution, was purified by recrystallisation from a mixture of acetone (1 vol.) and benzene (4 vols.). The crop weighed 5.6 grams, and gave the following value for the specific rotation in acetone :

$$l = 2, c = 2.10, \alpha_D - 2.61^\circ, [\alpha]_D - 62.1^\circ.$$

After two more recrystallisations from the same mixture of solvents, this value had only increased to -62.8° :

$$l = 2, c = 3.05, \alpha_D - 3.83^\circ, [\alpha]_D - 62.8^\circ.$$

Possibly *r*-mandelamide and *l*-mandelamide have the tendency to form mixed crystals.

Conversion of l-Mandelamide into l-Benzoin.

The preparation of *l*-benzoin by the action of magnesium phenyl bromide on *l*-mandelamide has been described by McKenzie and Wren (*loc. cit.*). Further experience has shown that it is not necessary to heat the mixture of amide and Grignard reagent for more than six hours instead of eight, as previously described. The crude reaction product, isolated as in previous experiments, possesses, after one recrystallisation from methyl alcohol, a specific rotation of approximately -110° in acetone solution, and is sufficiently pure to serve as the starting point for the preparation of derivatives of *l*-benzoin. Pure *l*-benzoin has $[\alpha]_D - 118.6^\circ$ in acetone. As the mean of many experiments, 10 grams of *l*-mandelamide have been found to yield 2.5 grams of *l*-benzoin.

Partly racemised *l*-benzoin cannot be purified by recrystallisation if its specific rotation falls below about -100° . An impure specimen having $[\alpha]_D - 82.9^\circ$, after one recrystallisation from methyl alcohol, had $[\alpha]_D - 87.8^\circ$, but after two further recrystallisations from the same solvent, this value had only increased to -88.8° .

In consequence of the partial racemisation which occurs when methyl *l*-mandelate is converted into *l*-mandelamide, and of the difficulty of purifying partly racemised specimens of *l*-mandelamide and *l*-benzoin, it is necessary to take special precautions that the methyl *l*-mandelate used as a starting point for the preparation of pure *l*-benzoin is as pure as possible. In one series of experiments, a specimen of methyl *l*-mandelate having $[\alpha]_D - 212.6^\circ$ ($c = 2.2715$) in carbon disulphide solution was employed. Successive preparations of

amide possessed $[\alpha]_D -64.7^\circ$ and -65.1° respectively when dissolved in acetone. These were converted into *l*-benzoin, which, after two recrystallisations from methyl alcohol, had $[\alpha]_D -101.8^\circ$, this value being increased to only -104.8° after another recrystallisation from the same solvent.

Racemisation of l-Benzoin.

Although *l*-benzoin is readily racemised by alkali, it does not appear to undergo autoracemisation. Thus *l*-benzoin (0.3599 gram) was dissolved in acetone, and the solution made up to 20 c.c. A portion of this solution, when examined in a 2-dcm. tube, had $\alpha_D -4.17^\circ$. The remainder was kept for a week. When brought into a 2-dcm. tube, its rotation was found to be identical with that of the first portion. Also a crystalline specimen of *l*-benzoin showed no change in activity during three months, the values for the specific rotation at the beginning and end of that period being respectively -115.9° and -116.3° .

The action of alkali on *l*-benzoin was studied in the following manner. *l*-Benzoin (1 gram) was boiled for thirty minutes with 50 c.c. of alcoholic potash (1 c.c. = 0.0065 gram KOH). The purple solution was poured into water (200 c.c.). After some time, the precipitated benzoin was collected and dried in a vacuum over sulphuric acid. Its solution in acetone was optically inactive. The crude product was recrystallised from methyl alcohol, after which it melted at $132.5-134^\circ$. In acetone solution it was optically inactive.

To a solution of *l*-benzoin (0.22 gram) in ethyl alcohol (20 c.c.), two drops of sodium ethoxide solution were added, after which it remained at the laboratory temperature during twenty-one hours. The solution was then poured into water, and the precipitated benzoin isolated as above. The latter was optically inactive when dissolved in acetone.

Racemisation of l-Benzoin Methyl Ether.

l-Benzoin methyl ether (0.2364 gram) was dissolved in cold alcoholic potash (0.113*N*) and the solution made up to 20 c.c. After an interval of five minutes, no optical activity could be detected ($l = 4$). Similarly a few drops of dilute sodium ethoxide solution were added to a solution of *l*-benzoin methyl ether in absolute ethyl alcohol. Five minutes after addition, the activity of the solution had diminished to two-thirds of its original value; after thirty minutes to rather less than a-half, whilst at the end of three and a-half hours no activity was observable.

Ethylation of l-Benzoin.

An attempt was made to prepare *l*-benzoin ethyl ether by Fischer's hydrochloric acid method, since Irvine and McNicoll (*Trans.*, 1908, 93,

1601) have shown that *r*-benzoin can be ethylated in this manner without the formation of by-products, such as were encountered when *r*-benzoin was methylated. It was found, however, that complete racemisation had occurred under the following conditions.

A solution of *l*-benzoin (2 grams) in dry ethyl alcohol (30 grams) was saturated with dry hydrogen chloride, first at 30—40° and subsequently at the temperature of the laboratory. After five days, the solution, which showed only feeble reducing action towards boiling Fehling's solution, was poured into water and the emulsion extracted with ether. The solid, obtained from the ethereal extract, was purified by crystallisation from boiling light petroleum, when 1.3 grams of substance were obtained, which, after a second crystallisation, melted at 60.5—61.5°. This product when dissolved in benzene yielded an optically inactive solution. The melting point of *r*-benzoin ethyl ether is given by Irvine and McNicoll (*loc. cit.*) as 62—63°, whereas Fischer (*Ber.*, 1893, 26, 2415) gives 62° and Lander (*Trans.*, 1900, 77, 733) 58—58.5°. On analysis :

0.1562 gave 0.4597 CO₂ and 0.0974 H₂O. C = 80.3 ; H = 7.0.

C₁₆H₁₆O₂ requires C = 80.0 ; H = 6.7 per cent.

Racemisation was shown to be complete by evaporating to dryness the mother liquor from the first recrystallisation and polarimetrically examining the solution of the residue in acetone.

It thus appears that *l*-benzoin and alcoholic hydrogen chloride interact to form *r*-benzoin ethyl ether.

The silver oxide method was next employed for the ethylation of *l*-benzoin. To a solution of *l*-benzoin (4 grams = 1 mol.) and ethyl iodide (26.5 grams = 9 mols.) in acetone (60 c.c.), dry silver oxide (13.1 grams = 3 mols.) was added. The mixture was cautiously heated to its boiling point and maintained at this temperature during two and a-half hours. After filtration from silver oxide and iodide and removal of acetone, an oil remained which had the odour of ethyl benzoate. Since it was possible that complete alkylation had not taken place, the product was dissolved in acetone (30 c.c.) and re-alkylated by treatment with half the above quantities of ethyl iodide and silver oxide. After removal of silver oxide, silver iodide, and acetone as before, an oil was obtained which could not be caused to crystallise. As it was conceivable that the oily nature of the product was due to the presence of ethyl benzoate, the latter was removed by steam distillation, but the residue could be obtained in no form other than an oil. It was accordingly distilled under diminished pressure. Under 6 mm. pressure a viscous, yellow oil of indefinite boiling point (up to 175°) was obtained, which slowly solidifies when placed in a freezing mixture. The solid was recrystallised from a small quantity

of boiling light petroleum. The whole filtrate, from which the crystals had been removed, when examined in a 1-dcm. tube had $\alpha_D + 8.08^\circ$. The crystals, which melted indefinitely at $54-61^\circ$, were polarimetrically examined in chloroform solution:

$$l = 2, c = 1.913, \alpha_D - 0.22^\circ, [\alpha]_D - 5.7^\circ.$$

The chloroform solution was evaporated to dryness, and the residue examined in heptane solution:

$$l = 2, c = 1.615, \alpha_D + 1.21^\circ, [\alpha]_D + 37.4^\circ.$$

The amount of substance was insufficient for further purification. It appears, therefore, that the product obtained was partly racemised *l*-benzoin ethyl ether, the optical properties of which are analogous to those of the methyl ether (see preceding paper). Racemisation is presumably due to the high temperature necessary for distillation, since it is improbable that the mechanism of methylation and ethylation by the silver oxide method differ, and in the former case a fully active product was readily isolated.

Racemisation of Carbanilido-l-benzoin.

It has been pointed out in the previous paper that carbanilido-*l*-benzoin melts at 121.5° , but solidifies again when heated slightly above this temperature, ultimately re-melting at 163.5° . The coincidence of this latter melting point with that of carbanilido-*r*-benzoin suggested that racemisation had taken place. To test this point, carbanilido-*l*-benzoin was heated in a soft glass tube for ten minutes at 130° and then for eight minutes at 150° . The product, which had solidified at the sides of the tube but not throughout the mass, was cooled and polarimetrically examined in acetone solution, when it proved to be but slightly racemised:

$$l = 2, c = 0.8065, \alpha_D - 3.35^\circ, [\alpha]_D - 207.7^\circ.$$

Pure carbanilido-*l*-benzoin has $[\alpha]_D^{21} - 214.8^\circ$ for $c = 0.6528$ in acetone.

The substance was therefore further heated during three and a-half hours at 140° , after which its solution in acetone was found to be optically inactive. It melted at about 163° .

In the above experiment, as also in the determination of the melting point, it was observed that the portions in contact with the glass were invariably the first to solidify, namely, to racemise. It would thus appear that racemisation is not conditioned solely by heat, but also by specific contact action of the glass.

Interaction of l-Benzoin and Aniline.

With the object of investigating the optical behaviour and action towards alkali of *l*-benzoinanilide, *l*-benzoin was condensed with aniline.

A mixture of *l*-benzoin (2.7 grams) with aniline (1.5 grams) was heated at 100° for four and a-half hours. The product melted at 97.5—99°, and was quite inactive. This melting point was practically unaltered by admixture with an approximately equal quantity of *r*-benzoinanilide (m. p. 98—99°) which had been prepared from *r*-benzoin and aniline. The product of the reaction was therefore *r*-benzoinanilide.

Interaction of l-Benzoin and Benzoyl Chloride.

The preparation of benzoyl-*r*-benzoin by heating together *r*-benzoin and benzoyl chloride has been described by Zinin (*Annalen*, 1857, 104, 116). An attempt was made to benzoylate *l*-benzoin in the same manner.

l-Benzoin (1.2 grams) was gently heated with re-distilled benzoyl chloride (2 grams). Evolution of hydrogen chloride started at 75°. After solution of the benzoin was complete at 100°, heating was continued in an oil-bath. Brisk evolution of hydrogen chloride occurred at 150°. The temperature was finally gradually raised to 195°, at which point gas evolution ceased. The cooled mixture was vigorously agitated with 75 per cent. alcohol (20 c.c.), whereupon it solidified. After three crystallisations from 80 per cent. alcohol, a well-crystallised product was obtained, which melted at 124—125° and was optically inactive in chloroform solution. Benzoyl-*r*-benzoin, according to Zinin, melts at 125°:

0.1779 gave 0.5199 CO₂ and 0.0777 H₂O. C = 79.7; H = 4.9.

C₂₁H₁₆O₃ requires C = 79.7; H = 5.1 per cent.

The substance obtained was therefore benzoyl-*r*-benzoin.

Acetylation of l-Benzoin- α -oxime.

l-Benzoin- α -oxime (1.6 grams) was covered with redistilled acetic anhydride (4 grams). With considerable development of heat, the oxime rapidly passed into solution, from which, on cooling, crystals separated. These were recrystallised from light petroleum (b. p. 60—80°), when colourless needles were obtained which melted at 86.5—87°. Their specific rotation was determined in benzene solution:

$$l = 4, c = 0.648, \alpha_D^{15} = -0.66^\circ, [\alpha]_D^{15} = -25.5^\circ.$$

In the light of the following observations, it is doubtful, however, if this product was optically pure.

In the hope of obtaining a better yield of the acetyl derivative, the experimental conditions were slightly altered in a second attempt. *l*-Benzoin-*a*-oxime (0.8 gram) was covered with acetic anhydride (2 grams). Solution of the oxime readily took place. After standing for thirty minutes, the mixture was placed in a vacuum desiccator over soda-lime in order to remove excess of acetic anhydride and acetic acid. The solid which remained was recrystallised from light petroleum. The colourless needles so obtained melted at 87.5–88°, and were polarimetrically examined in benzene solution :

$$l = 4, c = 0.974, \alpha_D^{16} = -0.85^\circ, [\alpha]_D^{16} = -21.8^\circ.$$

The observed angle did not change during twenty-one hours. After a second recrystallisation, the specific rotation was again determined in benzene solution :

$$l = 4, c = 0.7952, \alpha_D^{15} = -0.75^\circ, [\alpha]_D^{15} = -23.6^\circ.$$

Although the relative quantities of oxime and acetic anhydride were the same in both experiments, it will be observed that the product obtained in the second case was less active than in the first. This slight difference must be attributed to prolonged contact of the oxime, or more probably of its acetyl derivative, with acetic anhydride. A third experiment was made, in which the amount of the latter reagent was greatly reduced. A partly racemised product again resulted.

l-Benzoin-*a*-oxime (1.3 grams) was allowed to stand with acetic anhydride (1.1 grams) during fifteen minutes. The semi-solid reaction product was then brought into water, and the precipitated acetyl-*l*-benzoin-*a*-oxime collected, dried, and twice crystallised from boiling light petroleum. The colourless needles so obtained melted indefinitely at 89–96°. Their specific rotation was determined in benzene solution :

$$l = 4, c = 1.8452, \alpha_D^{17.2} = -1.15^\circ, [\alpha]_D^{17.2} = -15.6^\circ.$$

In this last experiment, owing to the reduction in the amount of acetic anhydride, the temperature attained by the reaction mixture was considerably higher than in the former cases. The extensive racemisation may be ascribed largely to this factor.

In conclusion, the author wishes to express his gratitude to Dr. Alex. McKenzie for the interest which he has taken in the work recorded in this and the preceding paper.

CLXXXI.—*Diketodiphenylpyrroline and its Analogues.*

By SIEGFRIED RUEHMANN.

It has recently been shown (this vol., 984) that, whilst the sodium compounds of fatty or fatty-aromatic amides react with ethyl phenylpropionate to form diacylimides, the metallic derivatives of benzamide or *o*-toluamide yield diketodiphenylpyrroline, $\begin{matrix} \text{CO} & \text{---} & \text{CO} \\ | & & | \\ \text{CPh} & \text{:} & \text{CPh} \end{matrix} \text{ > NH}$, or its

homologue respectively. It was stated, also, that this reaction seems to be typical of the behaviour of aromatic amides with ethyl phenylpropionate. The correctness of this view follows from the fact that analogues of diketodiphenylpyrroline are produced on using the sodium compounds of *m*- or *p*-toluamide, of cuminamide, anisamide, or piperonylamide. These substances have a deep colour, which varies from dark red to brown or black. The latter colour, accompanied by a beautiful metallic lustre, is characteristic of the diketopyrrolines which are formed from anisamide and piperonylamide. They all readily yield phenylhydrazones, which are orange, and differ only slightly in shade; these are sparingly soluble in cold alcohol, and this property, together with their melting points, may be used for isolating and identifying the diketopyrrolines, especially those which, on account of the ease with which they dissolve in alcohol, cannot readily be purified. The diketopyrrolines have the common property of dissolving in dilute alkalis to form blue solutions, which, however, rapidly turn yellow. This behaviour indicates their resemblance to isatin, and this is also shown in the similarity of the formation and the behaviour of their oximes. The oximes of diketodiphenylpyrroline and isatin are yellow; they both dissolve readily in alkalis to yield brown solutions. By the action of zinc dust and acetic acid, however, isatin yields isatide, $\text{C}_{16}\text{H}_{12}\text{O}_4\text{N}_2$, whereas the diketopyrroline combines with two atoms of hydrogen and forms the compound $\text{C}_{16}\text{H}_{13}\text{O}_2\text{N}$. This was regarded (*loc. cit.*) as diketodiphenylpyrrolidine, $\begin{matrix} \text{CO} & \text{---} & \text{CO} \\ | & & | \\ \text{CHPh} & \cdot & \text{CHPh} \end{matrix} \text{ > NH}$;

yet, a priori, the formula $\begin{matrix} \text{CH(OH) \cdot CO} \\ | \\ \text{CPh} = \text{CPh} \end{matrix} \text{ > NH}$ cannot be excluded.

According to the latter view, the reduction product would appear as an analogue of dioxindole, and therefore ought to resemble dioxindole and benzoin in properties. This, however, is not the case, for the latter compounds do not yield a colour reaction with ferric chloride, whereas the reduction product of diketodiphenylpyrroline gives a bluish-green coloration on the addition of ferric chloride to its

alcoholic solution. This fact proves the correctness of the view that the compound $C_{16}H_{13}O_2N$ is diketodiphenylpyrrolidine. This constitution, moreover, is supported by the following consideration. Diketodiphenylpyrrolidine may be represented by the tautomeric

formula: $\begin{array}{c} C(OH) \cdot C(OH) \\ | \quad | \\ CPh - CPh \end{array} \gg N$, which points to the relation of the com-

compound to catechol. This relation, indeed, exists, for both compounds give similar colorations with ferric chloride, are readily soluble in dilute alkalis, and reduce ammoniacal silver solutions. The presence of an ethylene linking in diketodiphenylpyrrolidine is proved, not only by the ease with which the substance combines with hydrogen, but also by its uniting with bromine to form dibromodiketodiphenyl-

pyrrolidine, $\begin{array}{c} CO \text{---} CO \\ | \quad | \\ CBrPh \cdot CBrPh \end{array} \gg NH$.

The results arrived at in the course of the study of the reaction of ethyl phenylpropiolate with amides induced me to investigate the behaviour of the acetylenic ester towards monosubstituted carbamides. That the latter substances, on treatment with sodium ethoxide, form metallic derivatives had been previously shown by Blacher (*Ber.*, 1895, **28**, 433) in the case of phenylcarbamide; these metallic compounds, however, do not condense with the ester to form cyclic substances, but acyl derivatives of carbamide are produced. This reaction, therefore, is similar to that between fatty or fatty-aromatic amides and ethyl phenylpropiolate (compare Ruhemann, this vol., 987). For the compound which is formed from phenylcarbamide, the following formulæ are possible:

$CPh:C \cdot CO \cdot NH \cdot CO \cdot NHPh$ (I.) or $CPh:C \cdot CO \cdot NPh \cdot CO \cdot NH_2$ (II.)

The first, however, according to which the sodium derivative of phenylcarbamide is to be represented by $C_6H_5 \cdot NH \cdot CO \cdot NH \cdot Na$ (III), appears to be more probable for the following reason. Some time ago, Ruhemann and Stapleton (*Trans.*, 1900, **77**, 239) showed that, in the presence of sodium ethoxide, carbamide reacts with ethyl phenylpropiolate to yield a yellow compound, which, from the fact that on boiling with potassium hydroxide it yields phenylpyruvic acid, has the constitution: $C_6H_5 \cdot CH:C \begin{array}{l} \text{CO} \text{---} \text{NH} \\ \text{NH} \cdot \text{CO} \end{array}$. Phenylpropiolylphenylcarbamide, however, is colourless, and behaves towards alkalis quite differently from benzylidenehydantoin. It follows, therefore, that the sodium derivative of phenylcarbamide is to be expressed by (III), and, accordingly, phenylpropiolylphenylcarbamide by (I); again, if sodio-phenylcarbamide had the formula $C_6H_5 \cdot NNa \cdot CO \cdot NH_2$, and the product of its reaction with ethyl phenylpropiolate the formula (II),

it was to be expected that it would condense to a cyclic compound similar to benzylidenedhydantoin.

EXPERIMENTAL.

Oxime of Diketodiphenylpyrroline, $\begin{matrix} \text{C}(\text{:NOH})\cdot\text{CO} \\ | \\ \text{CPh}=\text{CPh} \end{matrix} \text{>NH}$. — This

compound is readily formed by the method which Marchlewski (*Ber.*, 1896, 29, 1031) used for the preparation of isatoxime. For this purpose the pyrroline (1 gram) is dissolved in hot glacial acetic acid, and the solution, after the addition of hydroxylamine hydrochloride (0.5 gram) and an excess of sodium acetate, boiled for a short time. The deep red colour disappears, and a yellow solid separates. This is insoluble in water, sparingly soluble in ether, more readily so in boiling alcohol, and, on cooling the concentrated alcoholic solution, crystallises in small, yellow needles, which melt and decompose at 200—201°:

0.1497 gave 14 c.c. N_2 at 20° and 760 mm. $\text{N} = 10.69$.

$\text{C}_{16}\text{H}_{12}\text{O}_2\text{N}_2$ requires $\text{N} = 10.60$ per cent.

The oxime dissolves in cold dilute potassium hydroxide, as well as in sodium carbonate, yielding brown solutions, from which the oxime is precipitated unchanged on the addition of hydrochloric acid.

Dibromodiphenyldiketopyrrolidine, $\begin{matrix} \text{CO} \text{---} \text{CO} \\ | \\ \text{CBrPh}\cdot\text{CBrPh} \end{matrix} \text{>NH}$. — As pre-

viously stated, diketodiphenylpyrroline, on treatment with zinc dust and acetic acid, is reduced to diketodiphenylpyrrolidine. This readily dissolves in dilute potassium hydroxide to form a colourless solution, from which the pyrrolidine is precipitated on the addition of mineral acids. Diketodiphenylpyrroline also combines with bromine, and is transformed into the dibromo-derivative. This is prepared by adding bromine (0.6 gram) to the pyrroline (1 gram) dissolved in glacial acetic acid, when the deeply-coloured solution turns light red and, on pouring it into water, yields a solid. This is sparingly soluble in light petroleum, moderately so in hot alcohol or benzene, and, on adding light petroleum to its solution in benzene, is obtained in light brown needles which melt and decompose at 175°:

0.2305 gave 6.8 c.c. N_2 at 18° and 767 mm. $\text{N} = 3.44$.

0.2340 „ 0.2137 AgBr. $\text{Br} = 38.86$.

$\text{C}_{16}\text{H}_{11}\text{O}_2\text{NBr}_2$ requires $\text{N} = 3.42$; $\text{Br} = 39.12$ per cent.

Formation of Analogues of Diketodiphenylpyrroline.

These compounds have been prepared in the same way as diketodiphenylpyrroline, namely, by the action of ethyl phenylpropionate on

the sodium derivatives of aromatic amides. The latter products are obtained in a purer state by using metallic sodium in the form of wire than by evaporating in a vacuum a mixture of alcoholic solutions of the amides and sodium ethoxide. Absolute ether as a solvent is generally preferable to benzene, because the disappearance of the metal requires less time than in the presence of benzene, even in those cases where the amides are only sparingly soluble in ether. It is not necessary to use the large amount of the solvent which is required for their solution, but it is sufficient to digest the amide, suspended in ether, with the metal on the water-bath, when in the course of one to two days the sodium completely disappears.

2:3-Diketo-4-phenyl-5-*m*-tolylpyrroline, $\begin{matrix} \text{CO} & \text{---} & \text{CO} \\ | & & | \\ \text{CPh} & : & (\text{C}_6\text{H}_4\text{Me}) \end{matrix} \text{ > NH.}$ —On digesting ethyl phenylpropionate (9 grams) with sodio-*m*-toluamide, obtained by the action of sodium wire (1.2 grams) on the amide (7 grams), suspended in absolute ether, no reaction takes place until the ether is removed by distillation from the water-bath, when with the rise of temperature the whole becomes blue. To complete the reaction, the residue is boiled with dry benzene for an hour. After evaporation of the benzene, water is added, when the blue colour disappears. The solution which is formed is freed from unaltered amide and ethyl phenylpropionate by extraction with ether, and the aqueous layer saturated with carbon dioxide. A coloured, gelatinous solid is precipitated, which is removed by extraction with ether; finally, the yellow, aqueous solution which remains is treated with dilute hydrochloric acid, when the diketopyrroline is precipitated as a red oil which shortly sets to a solid. This dissolves readily in ether or hot alcohol, and, on cooling the alcoholic solution, crystallises in dark brown prisms, which melt at 150°, after having begun to soften a little before :

0.2205 gave 10.2 c.c. N_2 at 20° and 769 mm. $\text{N} = 5.35$.

$\text{C}_{17}\text{H}_{13}\text{O}_2\text{N}$ requires $\text{N} = 5.32$ per cent.

On boiling the diketopyrroline, dissolved in alcohol, with an excess of phenylhydrazine on the water-bath, the deep red solution turns light red, and, after a short time, the *phenylhydrazone* of diketophenyl-*m*-tolylpyrroline separates as a crystalline solid. This is scarcely soluble in cold, moderately so in boiling, alcohol, and crystallises in beautiful red needles, which melt and decompose at 217—218° :

0.2115 gave 21.8 c.c. N_2 at 20° and 769 mm. $\text{N} = 11.92$.

$\text{C}_{23}\text{H}_{19}\text{ON}_3$ requires $\text{N} = 11.90$ per cent.

2:3-Diketo-4-phenyl-5-*p*-tolylpyrroline, $\begin{matrix} \text{CO} & \text{---} & \text{CO} \\ | & & | \\ \text{CPh} & : & (\text{C}_6\text{H}_4\text{Me}) \end{matrix} \text{ > NH.}$ —This compound is prepared in the same way as its isomeride, namely,

by digesting *p*-toluamide (13.5 grams), suspended in absolute ether, with sodium wire (2.3 grams) until the metal has disappeared, and adding ethyl phenylpropiolate (17.4 grams). The reaction in this case, also, does not take place until the ether is removed and the mixture boiled with benzene for two to three hours on the water-bath. The blue residue which is left on distillation of the benzene is subjected to the same treatment as before, when a dark solid is obtained which dissolves readily in hot alcohol and separates in reddish-brown prisms; these are soluble in ether or benzene, and melt at 200°:

0.1788 gave 0.5070 CO₂ and 0.0815 H₂O. C = 77.33; H = 5.06,

0.2208 „ 10.4 c.c. N₂ at 19° and 764 mm. N = 5.44,

C₁₇H₁₃O₂N requires C = 77.57; H = 4.94; N = 5.32 per cent.

The *phenylhydrazone* separates as a red solid on digesting an alcoholic solution of the diketopyrroline with an excess of phenylhydrazine for half an hour on the water-bath. It dissolves in much boiling alcohol, and crystallises in red needles, which melt and decompose at 233—234°:

0.2095 gave 21.8 c.c. N₂ at 20° and 764 mm. N = 11.96.

C₂₃H₁₉ON₃ requires N = 11.90 per cent.

2:3-Diketo-4-phenyl-5-cumylpyrroline, $\begin{array}{c} \text{CO} \text{-----} \text{CO} \\ | \qquad \qquad \qquad | \\ \text{CPh} : \text{C}(\text{C}_6\text{H}_4 \cdot \text{C}_3\text{H}_7) \end{array} > \text{NH} \text{---}$

On adding ethyl phenylpropiolate (8.5 grams) to the magma of sodiocuminamide which is formed on digesting the amide (8.2 grams), suspended in absolute ether, with sodium wire (1.1 grams) for two days, no reaction takes place until, after the removal of the ether, the residue is heated on the water-bath alone or in the presence of benzene. The product, when subjected to the same treatment as before, yields the diketopyrroline, which readily dissolves in boiling alcohol and, on cooling the solution, crystallises in dark brown prisms. The substance is moderately soluble in ether, and melts at 185°:

0.1632 gave 0.4680 CO₂ and 0.0865 H₂O. C = 78.20; H = 5.89,

0.2195 „ 9.4 c.c. N₂ at 22° and 765 mm. N = 4.83,

C₁₉H₁₇O₂N requires C = 78.35; H = 5.84; N = 4.81 per cent.

The *phenylhydrazone* separates on boiling the alcohol solution of the diketopyrroline with phenylhydrazine on the water-bath. It is only sparingly soluble in cold, more readily so in boiling, alcohol, and crystallises in bunches of red needles, which melt at 217—218°:

0.2187 gave 21.4 c.c. N₂ at 21° and 757 mm. N = 11.10.

C₂₅H₂₃ON₃ requires N = 11.02 per cent.

2:3-Diketo-4-phenyl-5-anisylpyrroline, $\begin{array}{c} \text{CO} \text{-----} \text{CO} \\ | \qquad \qquad \qquad | \\ \text{CPh} : \text{C}(\text{C}_6\text{H}_4 \cdot \text{OMe}) \end{array} > \text{NH} \text{---}$

—Anisamide (7.6 grams), which, like the former amide, is prepared

in the usual way, namely, by the action of ammonium carbonate on anisoyl chloride, is transformed into its sodium derivative by suspending it in absolute ether and digesting it with sodium wire (1.2 grams). On adding ethyl phenylpropionate (8.7 grams), distilling off the ether, and boiling the residue with dry benzene, the mixture gradually turns blue, and, after two hours, the reaction is complete. The solid which is left on removal of the benzene by distillation from the water-bath is treated as in the former cases, and yields a dark precipitate. This is only sparingly soluble in ether or cold alcohol, moderately so in boiling alcohol, and, on cooling the deep red alcoholic solution, separates in prisms which, when small, are dark brown, but black when large, and then possess a metallic lustre. They melt and decompose at 254—255°:

0.2020 gave 0.5413 CO₂ and 0.0885 H₂O. C = 73.08; H = 4.86.

0.2200 „ 9.6 c.c. N₂ at 17° and 764 mm. N = 5.09.

C₇H₁₈O₃N requires C = 73.12; H = 4.66; N = 5.02 per cent.

The *phenylhydrazone* crystallises from alcohol in curved, red needles, which melt and decompose at 230°. It is formed in the same way as in the former cases, with the only exception that the diketopyrroline and phenylhydrazine must be used in molecular quantities, otherwise decomposition takes place.

2 : 3 - Diketo - 4 - phenyl - 5 - piperonylpyrroline, $\begin{array}{c} \text{CO} \text{---} \text{---} \text{CO} \\ | \qquad \qquad \qquad | \\ \text{CPh:C}(\text{C}_7\text{H}_5\text{O}_2) \end{array} \text{ > NH.}$

—Piperonylamide, which is required for the formation of this compound, was prepared according to the directions of Rupe and von Majewski (*Ber.*, 1900, **33**, 3403) by the action of hydrogen peroxide on piperonylonitrile in weakly alkaline solution. Its sodium derivative was prepared by the action of sodium wire (1.4 grams) on the amide (10.2 grams), suspended in dry benzene, two days' heating on the water-bath being necessary for the metal to disappear. On adding ethyl phenylpropionate (10.5 grams), hardly any change was noticeable even after two hours' boiling; a reaction, indicated by a blue coloration of the mixture, does not take place until, after the removal of the benzene by distillation from the water-bath, the temperature rises. The heating was continued for an hour, and the residue treated as before, when the diketopyrroline was obtained as a dark solid. This is only sparingly soluble in ether or cold alcohol, moderately so in boiling alcohol, and, on cooling the deep red alcoholic solution, gradually separates in black plates which possess a metallic lustre. The substance melts at 237—238°, after having begun to soften a few degrees before:

0.2000 gave 0.5102 CO₂ and 0.0710 H₂O. C = 69.57; H = 3.94.

0.2280 „ 9.8 c.c. N₂ at 21° and 754 mm. N = 4.85.

C₁₇H₁₁O₄N requires C = 69.62; H = 3.75; N = 4.78 per cent.

As in the previous case, for the preparations of the *phenylhydrazone* molecular quantities of the diketopyrroline and phenylhydrazine are used. After about an hour's heating of the alcoholic solution of the mixture, a red solid separates; this dissolves in much boiling alcohol, and, on cooling the solution, crystallises in deep red needles which melt and decompose at 250—251°:

0.2210 gave 21.4 c.c. N_2 at 21° and 755 mm. $N = 10.94$.

$C_{23}H_{17}O_3N_3$ requires $N = 10.97$ per cent.

Action of Ethyl Phenylpropiolate on Monoarylcabamides.

This reaction differs from that between carbamide and the acetylenic ester (see Ruhemann and Stapleton, *loc. cit.*) inasmuch as it does not yield cyclic compounds, but acyl derivatives of carbamide, which, as stated before (p. 1604), are to be represented thus:

$C_6H_5 \cdot C : C \cdot CO \cdot NH \cdot CO \cdot NHR$ (R denoting an aryl group).

Phenylpropiolylphenylcarbamide, $C_6H_5 \cdot C : C \cdot CO \cdot NH \cdot CO \cdot NH \cdot C_6H_5$.— This compound is readily prepared by mixing solutions of sodium (1.2 grams) and phenylcarbamide (6.8 grams) in absolute alcohol and distilling the solvent in a vacuum from the water-bath. To the sodium derivative of the carbamide which is formed, dry benzene and ethyl phenylpropiolate (9 grams) are added, and the mixture then boiled; after a short time, the whole sets to a semi-solid, white mass. The heating is continued for one to two hours, the benzene evaporated, and the residue agitated with ether, which removes unaltered phenylcarbamide and the acetylenic ester. The portion which is insoluble in ether contains the sodium derivative of phenylpropiolylphenylcarbamide; it dissolves, although not readily, in cold water, and the aqueous solution yields a white solid on the addition of dilute hydrochloric acid. This is sparingly soluble in ether or cold alcohol, but readily so in boiling alcohol, and crystallises in colourless, stout prisms, which melt at 205°:

0.1960 gave 0.5220 CO_2 and 0.0820 H_2O ; $C = 72.63$; $H = 4.64$.

0.2172 ,, 20 c.c. N_2 at 17° and 760 mm. $N = 10.63$.

$C_{16}H_{12}O_2N_2$ requires $C = 72.72$; $H = 4.54$; $N = 10.61$ per cent.

Phenylpropiolyl-p-tolylcarbamide, $C_6H_5 \cdot C : C \cdot CO \cdot NH \cdot CO \cdot NH \cdot C_6H_4 \cdot CH_3$, is prepared in the same way as the former compound on using *p*-tolylcarbamide; it is sparingly soluble in ether, readily so in boiling alcohol, and separates in colourless prisms, which melt at 192°:

0.2272 gave 20 c.c. N_2 at 17° and 753 mm. $N = 10.12$.

$C_{17}H_{14}O_2N_2$ requires $N = 10.07$ per cent.

The further study of the diketopyrrolines is in progress, and will be recorded shortly.

CLXXXII.—*isoQuinoline Derivatives. Part II. The Constitution of the Reduction Products of Papaverine.*

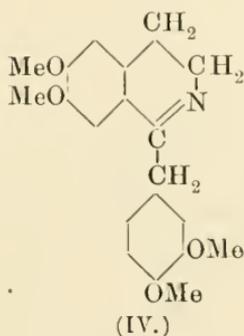
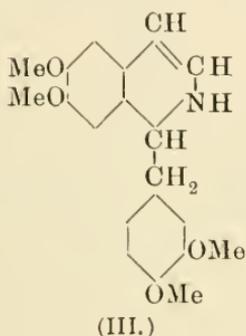
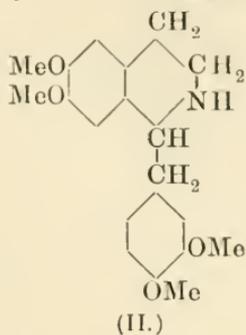
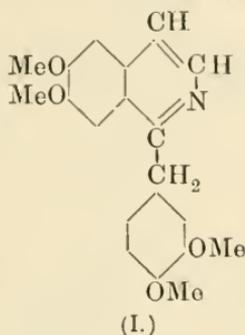
By FRANK LEE PYMAN.

IN a previous paper (this vol., p. 1266) it was shown that laudanosine can be readily oxidised to 4:5-dimethoxy-2- β -methylaminoethylbenzaldehyde by means of sulphuric acid and manganese dioxide, and it consequently became of interest to investigate the action of this reagent on other similarly constituted compounds, amongst others on the hitherto unknown *N*-benzoyltetrahydropapaverine. For this purpose, a quantity of tetrahydropapaverine was required, and the preparation of this compound was accordingly commenced by Goldschmiedt's method. This chemist (*Monatsh.*, 1886, **7**, 485; 1898, **19**, 324) obtained by the reduction of papaverine a crystalline base melting at 200—201° which he termed "tetrahydropapaverine," together with an amorphous base from which no crystalline derivative was obtained. Some years later, Freund and Beck (*Ber.*, 1904, **37**, 3321) obtained by the electrolytic reduction of papaveraldine an amorphous base, from which they prepared, through the nitrosoamine, a crystalline hydriodide; analyses of this salt were in agreement with the formula $C_{20}H_{25}O_4N, HI$, and they named the base provisionally "*isotetrahydropapaverine*," while pointing out that no such isomeride of Goldschmiedt's tetrahydropapaverine would be expected from consideration of Goldschmiedt's papaverine formula, and suggesting as an alternative that the base might have been formed by reduction and condensation of two molecules of papaveraldine to form a pinacone, and subsequent further reduction to a compound, $(C_{20}H_{24}O_4N)_2$.

It is shown in the present communication that the amorphous base resulting from the reduction of papaverine (I) is *tetrahydropapaverine* (II), and is identical with Freund and Beck's "*isotetrahydropapaverine*," and that Goldschmiedt's so-called "*tetrahydropapaverine*" is, in reality, a dihydropapaverine, namely, 6:7-dimethoxy-1-veratryl-1:2-dihydro*iso*quinoline, which it is proposed to designate 1:2-dihydropapaverine (III), in order to differentiate it from the 3:4-dihydropapaverine (IV) of Pictet and Finkelstein (*Ber.*, 1909, **42**, 1987).

The amorphous base obtained by the reduction of papaverine, either by Goldschmiedt's method, or more conveniently by the method given later, can be roughly separated from the crystalline base accompanying it by means of its easy solubility in ether, and

then purified through the hydriodide. It readily yields crystalline salts, of which the *hydrochloride*, *hydriodide*, *aurichloride*, and

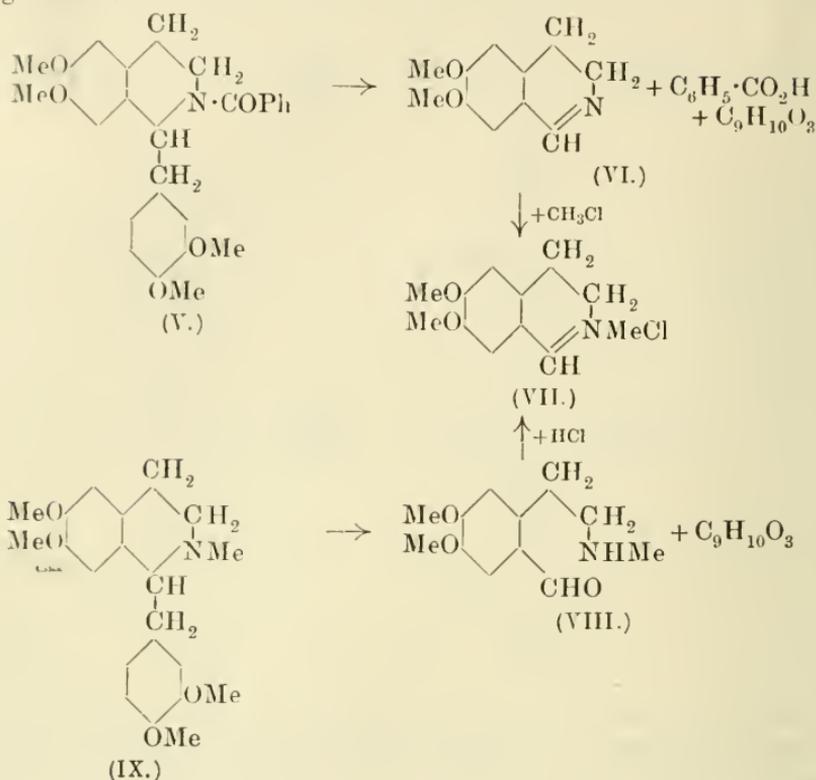


picrate have been prepared, and the analyses of these lead to the empirical formula of tetrahydropapaverine, $C_{20}H_{25}O_4N$, for this base; the amorphous nature of this base, the properties of its hydriodide, m. p. 259—260° (corr.), and those of its nitrosamine, m. p. 135—136° (corr.), show that it is identical with Freund and Beck's "*isotetrahydropapaverine*," of which the hydriodide is stated to melt at 255° and the nitrosamine at 138°.

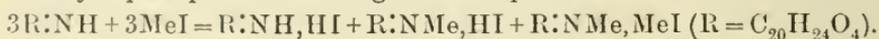
The amorphous base readily yields a crystalline *N-benzoyl* derivative, $C_{27}H_{29}O_5N$, of which the molecular weight has been determined, and shown to be that required by the simple formula, and the action of bromine on this benzoyl derivative in chloroform solution results in the formation of a crystalline *bromo-derivative*, $C_{27}H_{28}O_5NBr$.

The oxidation of the *N-benzoyl* derivative (V) leads to an important result, for there are formed benzoic acid, veratraldehyde, and a new base, 6:7-dimethoxy-3:4-dihydroisoquinoline (VI), the methochloride of which is identical with 6:7-dimethoxy-2-methyl-3:4-dihydroisoquinolinium chloride (VII). Since the latter compound has been obtained by the action of hydrochloric acid on 4:5-dimethoxy-2- β -methylaminoethylbenzaldehyde (VIII), which has been prepared by the oxidation of laudanosiue (IX) (*N*-methyl-tetrahydropapaverine), it follows that the amorphous base is

tetrahydropapaverine. This argument is illustrated by the following scheme:



The foregoing conclusion is further borne out by the fact that the amorphous base actually yields laudanidine on methylation. Freund and Beck (*loc. cit.*) state that the amorphous base yields, with methyl iodide in ethereal solution, crystals which are probably the hydriodide of the methylated base. The reaction is, however, less simple; on adding methyl iodide to an ethereal solution of tetrahydropapaverine, an amorphous deposit was obtained, which was separated by fractional crystallisation from alcohol into tetrahydropapaverine hydriodide, *laudanidine hydriodide*, and laudanidine methiodide, which appear to be formed in approximately equal parts according to the equation:



It is, therefore, proved beyond question that the amorphous base is tetrahydropapaverine.

Since Goldschmidt's papaverine formula only allows of the formation of one optically inactive tetrahydropapaverine, it is clear that this chemist's so-called "tetrahydropapaverine" must possess another constitution. Now, an examination of Goldschmidt's

analytical numbers shows that, whereas some of the results obtained by the analysis of the base and its derivatives are in good agreement with those calculated for the formula $C_{20}H_{25}O_4N$, others approximate more closely to those required by the formula $C_{20}H_{23}O_4N$. For example, the analyses of the hydrochloride and nitrosamine, as well as that of the base given in his second paper, show in round figures 0.3 per cent. of hydrogen less than that calculated for the formula $C_{20}H_{25}O_4N$. On the other hand, the analytical results obtained by Pope and Peachey (*Trans.*, 1898, **73**, 893) for the racemic and optically active forms of this base are in excellent agreement with this formula. It was therefore necessary to reinvestigate this base. The base, its hydrochloride, and *N*-benzoyl derivative were accordingly carefully purified and analysed, when the results obtained decided definitely in favour of the formula $C_{20}H_{23}O_4N$. Further, the corresponding papaveroline derivative was also prepared by the removal of the four methyl groups, and its *hydrochloride* gave, on analysis, figures agreeing with those required by the formula $C_{16}H_{15}O_4N, HCl$, corresponding with the formula of the methylated compound $C_{20}H_{23}O_4N$; *tetrahydropapaveroline hydrochloride*, on the other hand, which was prepared from tetrahydropapaverine for the purpose of comparison, gave, on analysis, figures agreeing with the expected formula $C_{16}H_{17}O_4N, HCl$, corresponding with the formula of the methylated compound $C_{20}H_{25}O_4N$; this result is important, since the difference in hydrogen content between the formulæ of the two hydrochlorides amounts to 0.6 per cent. A determination of the molecular weight of the base proved it to have the simple formula. The only possible conclusion from these facts is that this crystalline base obtained by the reduction of papaverine is a dihydropapaverine, and, since Pope and Peachey (*loc. cit.*) have resolved it into its optically active forms, and thereby shown that it contains a hydrogen atom in the 1-position, and Goldschmiedt has prepared a nitrosoamine from it, thus proving it to contain an imino-group, this base must consequently be 1:2-dihydropapaverine.

1:2-Dihydropapaverine is a compound of considerable stability, and has thus far resisted attempts to effect its reduction. In this respect it differs from a compound of similar type, 1-benzyl-2-methyl-1:2-dihydroisoquinoline, recently described by Freund and Bode (*Ber.*, 1909, **42**, 1762), which readily yields 1-benzyl-2-methyltetrahydroisoquinoline when reduced with tin and hydrochloric acid, although the reduction is incomplete when sodium and alcohol are employed. This difference in behaviour between 1:2-dihydropapaverine and 1-benzyl-2-methyl-1:2-dihydroisoquinoline must probably be ascribed to the presence of the free

imino-group in the former, and this view is supported by the fact that the unknown *N*-methyl ether of 1:2-dihydropapaverine has not been obtained in the reduction of papaverine methochloride, in which hitherto only laudanosine has been isolated (Pictet and Athanasescu, *Ber.*, 1900, **33**, 2346).

N-Benzoyl-1:2-dihydropapaverine is also a very stable compound; it is not readily attacked either by bromine or by sulphuric acid and manganese dioxide, thus differing markedly from *N*-benzoyl-tetrahydropapaverine.

EXPERIMENTAL.

Reduction of Papaverine.

One hundred grams of papaverine were dissolved in a mixture of 400 c.c. of alcohol and 400 c.c. of concentrated hydrochloric acid, and boiled with 200 grams of granulated tin under a reflux condenser for five hours. Further quantities of 50 grams of tin and 200 c.c. of hydrochloric acid were then added, and the mixture boiled for another seven hours. The alcohol was then removed by distillation, and the acid liquor cooled and diluted with water, which caused the precipitation of double salts of tin and the alkaloids in a white, amorphous condition. These were collected, washed with water, dissolved in 3 litres of boiling water, and decomposed with hydrogen sulphide. The resulting solution of the hydrochlorides was filtered from tin sulphide, rendered strongly alkaline with sodium carbonate, and completely extracted, first with ether, and then with chloroform.

The ethereal residue amounted to 65 grams of sticky oil; this dissolved to a clear solution in dilute hydrochloric acid, and the solution gave, on the addition of solid potassium iodide, an amorphous precipitate, which became crystalline after boiling with absolute alcohol, and furnished 55 grams of pure tetrahydropapaverine hydriodide, melting at 259—260° (corr.).

The chloroform residue amounted to about 15 grams of a brown, viscid oil, and gave 14 grams of a crystalline hydrochloride when mixed with dilute hydrochloric acid. On dissolving this in water, adding aqueous sodium carbonate, and recrystallising the separated base from absolute alcohol, more than 8 grams of 1:2-dihydropapaverine, melting at 201—202° (corr.), were obtained.

The mother liquors obtained in the purification of the two bases contained further quantities of these compounds.

Tetrahydropapaverine (II, p. 1611).

This base has only been obtained in an amorphous form; it remains as a colourless, viscid gum on the evaporation of its

solutions in various solvents. It is moderately readily soluble in water, insoluble in light petroleum, and readily soluble in the other usual organic solvents. On dissolving this base in hydrochloric acid and adding an excess of sodium nitrite solution, tetrahydropapaverinenitrosoamine separates as a sticky oil, which becomes crystalline on stirring with alcohol, and separates from alcohol in short needles which melt at 135—136° (corr.).

Tetrahydropapaverine forms beautifully crystalline salts.

The hydriodide, of which the preparation has already been described, crystallises from water in prisms which melt at 259—260° (corr.) after becoming yellow a few degrees below this point. This salt is anhydrous, and is very sparingly soluble in water or alcohol:

0·1512 gave 0·2832 CO₂ and 0·0748 H₂O. C=51·1; H=5·5.

0·1885 „ 0·0942 AgI. I=27·0.

C₂₀H₂₅O₄N,HI requires C=51·0; H=5·6; I=27·0 per cent.

The *hydrochloride* was obtained by double decomposition of the hydriodide with silver chloride; it crystallises from water in glistening prisms, which sinter at 81° and melt at 83—85° (corr.) to an opaque liquid, and contains 4½ molecules of water of crystallisation, of which 3½ are lost at 100°. After recrystallisation from absolute alcohol, this salt is obtained as an anhydrous, crystalline powder, which melts at 217—219° (corr.). It is sparingly soluble in water, and very sparingly so in alcohol:

0·6950 hydrated salt, air-dried, lost 0·0967 at 100°. H₂O=13·9.

0·1610 „ „ dried at 100°, gave 0·3590 CO₂ and 0·0977 H₂O.

C=60·8; H=6·8.

C₂₀H₂₅O₄N, HCl, 4½H₂O, losing 3½H₂O, requires loss=13·7 per cent.

C₂₀H₂₅O₄N, HCl, H₂O requires C=60·3; H=7·1.

0·1527 anhydrous salt gave 0·3540 CO₂ and 0·0953 H₂O. C=63·2; H=7·0.

0·1900 anhydrous salt gave 0·0699 AgCl. Cl=9·1.

C₂₀H₂₅O₄N, HCl requires C=63·2; H=6·9; Cl=9·3 per cent.

The *aurichloride* crystallises from absolute alcohol in radial clusters of deep yellow needles, which blacken and decompose at 176° (corr.). This salt is anhydrous, and is very sparingly soluble in water and sparingly so in alcohol:

0·2546 gave 0·0739 Au. Au=29·0.

C₂₀H₂₅O₄N, HAuCl₄ requires Au=28·9 per cent.

The *picrate* crystallises from absolute alcohol in clear, yellow, irregular prisms, which begin to sinter at 155° and decompose at 161—162° (corr.). This salt gradually becomes orange superficially; it is anhydrous, and is very sparingly soluble in water or alcohol:

0.1295 gave 0.2578 CO₂ and 0.0536 H₂O. C=54.3; H=4.6.

C₂₀H₂₅O₄N, C₆H₃O₇N₃ requires C=54.5; H=4.9 per cent.

Methylation of Tetrahydropapaverine.

Seventeen grams of pure tetrahydropapaverine hydriodide were mechanically shaken with 100 c.c. of chloroform and 100 c.c. of 10 per cent. aqueous sodium carbonate for fifteen minutes, and the chloroform solution evaporated to low bulk. The residue was mixed with 50 c.c. of moist ether, and 15 grams of methyl iodide were then added. The solution became turbid almost immediately, and deposited a light brown, amorphous solid. After twelve hours, the supernatant liquor was poured off, and gave, on evaporation, 0.4 gram of light brown oil, which was added to the solid residue. The amorphous deposit was fractionally extracted with boiling absolute alcohol, and the various crops of crystals obtained from the extracts were separated by fractional crystallisation, and gave the following products:

(1) 4.8 Grams of tetrahydropapaverine hydriodide. This salt melted at 259—260° (corr.), and its melting point suffered no depression when the salt was mixed with the pure substance:

0.1520 gave 0.2860 CO₂ and 0.0771 H₂O. C=51.3; H=5.7.

0.1978 „ 0.0984 AgI. I=26.9.

C₂₀H₂₅O₄N, HI requires C=51.0; H=5.6; I=27.0 per cent.

(2) 4.8 Grams of laudanosine methiodide. This salt melted at 213—215° (corr.), and its melting point suffered no depression when the salt was mixed with the pure substance:

0.1519 gave 0.2945 CO₂ and 0.0825 H₂O. C=52.9; H=6.1.

0.1519 „ 0.0726 AgI. I=25.8.

C₂₁H₂₇O₄N, CH₃I requires C=52.9; H=6.0; I=25.5 per cent.

(3) 1.1 Grams of *laudanosine hydriodide*. This salt melted at 201—203° (corr.), and its melting point suffered no depression when the salt was mixed with the pure substance prepared by neutralising laudanosine with hydriodic acid. This salt is anhydrous, and is sparingly soluble in water or cold absolute alcohol:

0.1534 gave 0.2900 CO₂ and 0.0814 H₂O. C=51.6; H=5.9.

0.2010 „ 0.0965 AgI. I=25.9.

C₂₁H₂₇O₄N, HI requires C=51.9; H=5.8; I=26.2 per cent.

Besides the above quantities of pure salts, a number of fractions consisting of mixtures were obtained. These were combined, dissolved in water, and mixed with aqueous sodium carbonate; this caused the precipitation of 2.0 grams of a brown oil, which solidified on cooling, and proved to contain a large proportion of laudanosine.

N-Benzoyltetrahydropapaverine (V, p. 1612).

This compound was prepared by benzoylating tetrahydropapaverine in a manner similar to that applied to 1:2-dihydropapaverine.

N-Benzoyltetrahydropapaverine crystallises from absolute alcohol in clusters of glistening, prismatic needles, which melt at 159—160° (corr.). It is very sparingly soluble in water or ether, sparingly so in acetone or alcohol, but readily so in chloroform. It is insoluble in dilute acids or alkalis:

0.1527 gave 0.4050 CO₂ and 0.0911 H₂O. C = 72.3; H = 6.7.

0.1538 „ 4.2 c.c. N₂ at 22° and 754 mm. N = 3.1.

C₂₇H₂₉O₅N requires C = 72.4; H = 6.5; N = 3.1 per cent.

Molecular weight determination by the ebullioscopic method:

0.2270 in 12.37 benzene gave Δ*t* 0.110. M.W. = 445.

0.4070 „ 12.37 „ „ Δ*t* 0.195. M.W. = 451.

C₂₇H₂₉O₅N requires M.W. = 447.

Bromo-N-benzoyltetrahydropapaverine, C₂₇H₂₈O₅NBr.

Two grams of *N*-benzoyltetrahydropapaverine were dissolved in 20 c.c. of chloroform, and a solution of 1 gram of bromine in 30 c.c. of chloroform was added. The mixture was kept for forty hours, and then allowed to evaporate spontaneously; the gummy residue was dissolved in a little alcohol, and mixed with aqueous ammonia, when 2.2 grams of bromo-*N*-benzoyltetrahydropapaverine separated as an oil, which became crystalline on keeping; this yield represents 93 per cent. of the theoretical.

Bromo-N-benzoyltetrahydropapaverine crystallises from absolute alcohol in clusters of colourless, square leaflets, which melt at 185—186° (corr.); it is insoluble in water, dilute acids, or alkalis, and sparingly soluble in cold alcohol:

0.1456 gave 0.3303 CO₂ and 0.0721 H₂O. C = 61.9; H = 5.5.

0.1961 „ 0.0706 AgBr. Br = 15.3.

C₂₇H₂₈O₅NBr requires C = 61.6; H = 5.4; Br = 15.2 per cent.

Oxidation of N-Benzoyltetrahydropapaverine: Formation of 6:7-Dimethoxy-3:4-dihydroisoquinoline (VI, p. 1612).

Thirty-five grams of *N*-benzoyltetrahydropapaverine, melting at 159—160° (corr.), were ground to a fine powder with 200 c.c. of water, mixed with a solution of 70 grams of sulphuric acid in 1 litre of water and 17.5 grams of pyrolusite, containing 80 per cent. of manganese dioxide, and well stirred. The temperature

was gradually raised to the full heat afforded by the steam-bath, and after one hour the suspension had given place to a nearly clear, pale yellow liquor containing a quantity of resinous matter. The latter was removed by filtration; it weighed 18 grams, of which 3 grams consisted of inorganic material, and gave 9 grams of unchanged *N*-benzoyltetrahydropapaverine after crystallisation from alcohol; the sticky mother liquors from this were neglected.

The filtrate from the resinous matter was completely extracted with ether, and this in turn with aqueous sodium carbonate; the ether left on evaporation 5.5 grams of crude veratraldehyde, and the alkaline extract gave on acidification 4.5 grams of benzoic acid.

The aqueous solution of the basic products was then rendered alkaline with sodium carbonate, and completely extracted with chloroform; on then adding sodium hydroxide and again extracting with chloroform, no further quantity of material was obtained.

The chloroform extract from the sodium carbonate solution gave on distillation a quantity of brown oil, which was purified by distillation under 24 mm. pressure, when more than 5 grams of 6:7-dimethoxy-3:4-dihydroisoquinoline distilled at 205—208° (corr.), and formed a viscid, yellow oil with a faint blue fluorescence, which did not crystallise on keeping:

0.1948 gave 0.4905 CO₂ and 0.1250 H₂O. C=68.7; H=7.2.

C₁₁H₁₃O₂N requires C=69.1; H=6.9 per cent.

6:7-Dimethoxy-3:4-dihydroisoquinoline is readily soluble in water and the usual organic solvents, with the exception of light petroleum. It forms crystalline salts with acids, and combines with methyl halides in ethereal solution, forming methyl salts which are identical with the salts obtained by the action of the corresponding acids on 4:5-dimethoxy-2-β-methylaminoethylbenzaldehyde.

The base is precipitated as an oil on the addition of aqueous sodium carbonate to concentrated solutions of its salts. The addition of aqueous potassium cyanide to the hydrochloride in concentrated aqueous solution causes the separation of an oil, which is no doubt 1-cyano-6:7-dimethoxytetrahydroisoquinoline.

The hydrochloride crystallises from aqueous acetone in pale yellow, glistening needles, which melt at 72—75° (corr.), and contain 3 molecules of water of crystallisation. After drying at 100°, this salt melts and decomposes at 208° (corr.). It is very readily soluble in water or alcohol, giving neutral solutions, which, when dilute, show a blue fluorescence, but insoluble in acetone:

0.1548, air-dried salt, gave 0.2685 CO₂ and 0.0983 H₂O. C=47.3; H=7.1.

0.2051, air-dried salt, gave 0.1070 AgCl. Cl=12.9.

0.2020, air-dried salt, lost 0.0380 at 100°. $H_2O = 18.8$.

$C_{11}H_{13}O_2N, HCl, 3H_2O$ requires $C = 46.9$; $H = 7.2$; $Cl = 12.6$;
 $H_2O = 19.2$ per cent.

0.1500, dried at 100°, gave 0.3197 CO_2 and 0.0868 H_2O . $C = 58.1$;
 $H = 6.5$.

$C_{11}H_{13}O_2N, HCl$ requires $C = 58.0$; $H = 6.2$ per cent.

The *picrate* crystallises from absolute alcohol in fine, golden, silky needles, which melt at 206—208° (corr.), after sintering several degrees earlier.

The *methochloride* was obtained as follows. An ethereal solution of 6:7-dimethoxy-3:4-dihydroisoquinoline was mixed with methyl iodide, when a deep yellow oil, which quickly became crystalline, separated. This was dissolved in water and shaken with silver chloride; the resulting liquor was filtered, evaporated to low bulk, and mixed with acetone, when the methochloride separated as a yellow, crystalline powder, which melted at 61—62° (corr.), and proved to be identical with 6:7-dimethoxy-2-methyl-3:4-dihydroisoquinolinium chloride.*

The *methobromide* was prepared directly by the action of methyl bromide on the base in ethereal solution; after recrystallisation from moist acetone it formed primrose needles, which sintered at 87—90° (corr.), both alone and when mixed with 6:7-dimethoxy-2-methyl-3:4-dihydroisoquinolinium bromide prepared from 4:5-dimethoxy-2- β -methylaminoethylbenzaldehyde.

Tetrahydropapaveroline, $C_{16}H_{17}O_4N$.

Five grams of tetrahydropapaverine hydrochloride, containing $4\frac{1}{2}H_2O$, were heated with 50 c.c. of concentrated hydrochloric acid for three hours at 170—175°. On opening the tube, methyl chloride escaped, and a clear liquid containing brown, serrated needles remained; the latter were collected and weighed 3.5 grams, that is, 97 per cent. of the theoretical.

Tetrahydropapaveroline hydrochloride crystallises from water in colourless, microscopic, glistening prisms, which melt and decompose at 291—293° (corr.), after gradually sintering and turning yellow from about 280°. It is very sparingly soluble in water or alcohol, and is anhydrous:

0.1509 gave 0.3266 CO_2 and 0.0764 H_2O . $C = 59.0$; $H = 5.7$.

0.1764 „ 0.0793 $AgCl$. $Cl = 11.1$.

$C_{16}H_{17}O_4N, HCl$ requires $C = 59.3$; $H = 5.6$; $Cl = 11.0$ per cent.

* The statement (this vol., p. 1271) that this salt crystallises “from aqueous solution in a mass of primrose needles . . .” should read “from aqueous acetone in a mass of primrose needles . . .”

This salt readily reduces cold ammoniacal silver nitrate solution, and liberates cuprous oxide from Fehling's solution on boiling. It gives with ferric chloride, in the first instance, a deep green colour, which quickly passes through a neutral tint to amethyst; on the addition of aqueous sodium carbonate, black flakes are deposited, and the supernatant liquor becomes colourless.

Concentrated solutions of this salt give with alkalis a white turbidity, due to the corresponding base; this is soluble in excess, giving a pale amethyst coloration; alkaline solutions, however, very quickly blacken when left in contact with air.

1: 2-Dihydropapaverine (III, p. 1611).

This base has previously been described by Goldschmiedt under the name tetrahydropapaverine, and is stated to be precipitated from the solution of its hydrochloride on the addition of ammonia in anhydrous needles, and to melt at 200—201°, after sintering at 198°. It has now been found, however, that the colourless needles obtained by the addition of ammonia to an aqueous solution of the hydrochloride, whether this is prepared by the above method or by Goldschmiedt's, represent a hydrated form of the base, containing 3H₂O, which, after air-drying, sinters at 65°, and finally melts at 201—202° (corr.):

0.2062, air-dried precipitated base, lost 0.0295 at 110°. H₂O = 14.3.

C₂₀H₂₃O₄N, 3H₂O requires H₂O = 13.7 per cent.

0.1673, dried at 110°, gave 0.4305 CO₂ and 0.1038 H₂O. C = 70.2; H = 7.0.

C₂₀H₂₃O₄N requires C = 70.3; H = 6.8 per cent.

(C₂₀H₂₅O₄N ,, C = 70.0; H = 7.3 ,, ,)

After crystallising this base from alcohol, it becomes anhydrous, and melts at 201—202° (corr.); this melting point is unchanged by crystallising the base from xylene, from which it separates in large prisms. For analysis, the base was recrystallised, first from alcohol, and then from xylene, and dried at 110°:

0.1549 gave 0.4016 CO₂ and 0.0972 H₂O. C = 70.7; H = 7.0.

0.1516 ,, 0.3918 CO₂ ,, 0.0915 H₂O. C = 70.5; H = 6.8.

Molecular weight determination by the ebullioscopic method:

0.1439 in 12.05 benzene gave Δt 0.090. M.W. = 354.

0.3556 ,, 12.05 ,, ,, Δt 0.230. M.W. = 343.

C₂₀H₂₃O₄N requires M.W. = 341.

The hydrochloride is stated by Goldschmiedt to decompose at 290°, and contain 3 molecules of water of crystallisation, of which 1½ are gradually lost in dry air. After preparing this salt from the carefully purified base, it was found, however, to decompose

at about 325° (corr.). It forms beautifully crystalline rods from water, which contain 5 molecules of water of crystallisation; this salt has also been obtained with 8H₂O:

0.4012 air-dried lost 0.0789 at 110°. H₂O=19.7.

C₂₀H₂₃O₄N, HCl, 5H₂O requires H₂O=19.3 per cent.

0.2134 air-dried lost 0.0592 at 100°. H₂O=27.7.

C₂₀H₂₃O₄N, HCl, 8H₂O requires H₂O=27.6 per cent.

0.1544, dried at 110°, gave 0.3567 CO₂ and 0.0895 H₂O. C=63.0;
H=6.5.

0.1511, dried at 110°, gave 0.3505 CO₂ and 0.0874 H₂O. C=63.3;
H=6.5.

0.1527, dried at 110°, gave 0.0562 AgCl. Cl=9.1.

C₂₀H₂₃O₄N, HCl requires C=63.5; H=6.4; Cl=9.4 per cent.

(C₂₀H₂₅O₄N, HCl ,, C=63.2; H=6.9; Cl=9.3 per cent.)

The picrate was prepared from the pure hydrochloride in the usual manner, and formed long, yellow needles, which began to darken at 270°, and decomposed at 285° (corr.). Goldschmiedt states that this salt turns black at 245°, and decomposes at 270°.

Attempts to effect the reduction of 1:2-dihydropapaverine by means of (1) tin and fuming hydrochloric acid in alcoholic solution, and (2) sodium and alcohol, proved unsuccessful; in each case the base was recovered unchanged.

N-Benzoyl-1:2-dihydropapaverine, C₂₇H₂₇O₅N.

Five and a-half grams of 1:2-dihydropapaverine were benzoylated in chloroform solution by the Schotten-Baumann method; the resulting chloroform solution of the benzoyl derivative was mechanically shaken with a large excess of 10 per cent. aqueous sodium hydroxide, separated, dried, and evaporated. The brown oil obtained was then moistened with alcohol and again evaporated in an open dish, this process being repeated a second time, and then dissolved in about twice its volume of absolute alcohol. On cooling, 4.9 grams of pure *N*-benzoyl-1:2-dihydropapaverine separated as a crystalline powder, the yield amounting to 68 per cent. of the theoretical.

N-Benzoyl-1:2-dihydropapaverine crystallises from absolute alcohol in colourless, transparent, glistening prisms, which melt at 234—235° (corr.). It is very sparingly soluble in water or ether, sparingly so in alcohol or acetone, and readily so in chloroform:

0.1542 gave 0.4101 CO₂ and 0.0856 H₂O. C=72.5; H=6.2.

0.1530 ,, 4.2 c.c. N₂ at 24° and 774 mm. N=3.1.

C₂₇H₂₇O₅N requires C=72.7; H=6.1; N=3.1 per cent.

On leaving this substance in contact with bromine (2 atoms to 1 molecule) in chloroform solution for forty hours, allowing the chloroform to evaporate, dissolving the residue in a little alcohol, precipitating it with dilute aqueous ammonia, and crystallising the precipitate from alcohol, a considerable proportion is recovered unchanged; after the evaporation of the alcohol, the residue forms a yellow gum, which does not contain bromine.

On attempting to oxidise *N*-benzoyl-1:2-dihydropapaverine with dilute sulphuric acid and manganese dioxide under the conditions previously described for *N*-benzoyltetrahydropapaverine, more than 70 per cent. was recovered unchanged, and no crystalline degradation products were obtained except a trace of benzoic acid.

1:2-Dihydropapaveroline, $C_{16}H_{15}O_4N$.

This compound has previously been described by Goldschmiedt under the name "tetrahydropapaveroline." Comparison of the colour reactions given here for 1:2-dihydropapaveroline and tetrahydropapaveroline with those given by Goldschmiedt (*loc. cit.*) for his compound indicate that the latter probably contained a certain amount of tetrahydropapaveroline.

Three grams of 1:2-dihydropapaverine hydrochloride (containing $8H_2O$) were heated with 30 c.c. of concentrated hydrochloric acid for three hours at $170-175^\circ$. On opening the tube, methyl chloride escaped, and a pale yellow liquid containing pale brown crystals remained; the latter were collected, and weighed 1.4 grams, that is, 74 per cent. of the theoretical.

1:2-Dihydropapaveroline hydrochloride crystallises from water in nearly colourless prisms, which decompose at 296° (corr.). This salt contains half a molecular proportion of water of crystallisation, and is easily soluble in water:

0.2750 air-dried lost 0.0095 at 120° . $H_2O = 3.5$.

0.1734, dried at 120° , gave 0.3783 CO_2 and 0.0798 H_2O . $C = 59.5$;
 $H = 5.2$.

0.1530, dried at 120° , gave 0.3349 CO_2 and 0.0689 H_2O . $C = 59.7$;
 $H = 5.0$.

$C_{16}H_{15}O_4N, HCl, \frac{1}{2}H_2O$ requires $H_2O = 2.7$ per cent.

$C_{16}H_{15}O_4N, HCl$ requires $C = 59.7$; $H = 5.0$ per cent.

This salt readily reduces cold ammoniacal silver nitrate solution, but does not liberate cuprous oxide from Fehling's solution on boiling. It gives with ferric chloride a persistent, deep green colour, and, on the addition of aqueous sodium carbonate, dark flakes are deposited, leaving a violet-coloured supernatant liquor.

Concentrated solutions of this salt give with alkalis a white precipitate, which is soluble in excess, giving a pale yellowish-green solution; alkaline solutions, however, very quickly blacken on exposure to air.

THE WELLCOME CHEMICAL WORKS,
DARTFORD, KENT.

CLXXXIII.—*The Synthesis of Acridines: Tetramethylacridines, Dimethylnaphthacridines, Naphthaquinacridines, Diquinacridines.**

By ALFRED SENIER and ARTHUR COMPTON.

THE experiments described in this paper were undertaken with the object of effecting a linking of two heterocyclic groups, or one heterocyclic and one carbocyclic group, with an acridine nucleus by using the first and second of the methods described in a previous paper (Trans., 1907, 91, 1927), and also to extend the work therein reported on the synthesis of alkylacridines and phenonaphthacridines. We have succeeded in obtaining a new tetramethylacridine and the corresponding dimethylpheno- α - and - β -naphthacridines, and by the use of 6-aminoquinoline we have prepared and isolated one di- and two mono-heterocyclic acridines. The constitution of these bases follows from their modes of formation, as in the case of simpler acridines and naphthacridines, and the notation employed is that previously made use of, adapted in the case of quinoline derivatives to the usual notation employed for those compounds (compare Senier and Austin, Trans., 1904, 85, 1196, footnote; 1906, 89, 1387; 1907, 91, 1240).

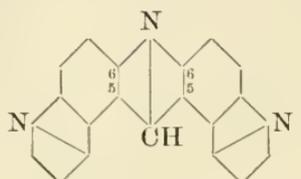
The positions of the methyl groups in the tetramethylacridine described are 2:3:7:8, and the phenonaphthacridines are 9:10-

dimethylpheno- $\overset{\text{N-}\alpha}{\underset{\text{CH-}\beta}{|}}$ -naphthacridine and 9:10-dimethylpheno-

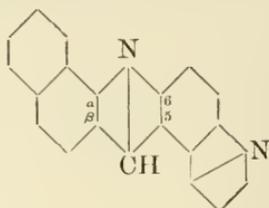
$\overset{\text{N-}\beta}{\underset{\text{CH-}\alpha}{|}}$ -naphthacridine of the types represented respectively by diagrams *A* and *B* in a previous paper (Trans., 1907, 91, 1241).

* The nomenclature is adopted in accordance with that employed in this Journal for the analogous dinaphthacridines and phenonaphthacridines, notwithstanding that the name *quinaacridine* has been already made use of for compounds of a different type by previous observers (Niemętowski, *Ber.*, 1896, 29, 78; 1906, 39, 385; Ullmann and Broido, *Ber.*, 1906, 39, 357).

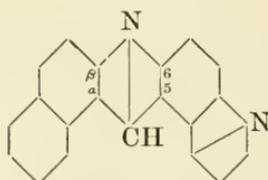
The constitution of the quinoline derivatives may be represented thus:



6-N-6
|
5-CH-5 -Diquinacridine.



alpha-N-6
|
beta-CH-5 -Naphthaquinacridine.



beta-N-6
|
alpha-CH-5 -Naphthaquinacridine.

In assigning the constitution to the compounds indicated by the above formulæ, it is assumed that the 5-position in 6-aminoquinoline is more active than the 7-position, and that condensation takes place there as in the case of the corresponding α -position in β -naphthylamine.

6-N-6
|
5-CH-5-Diquinacridine is the first known member of a group of diquinacridines, of which twenty other members are theoretically possible, all derived from ordinary quinoline; and, similarly, sixteen other isomeric naphthaquinacridines are possible in the group represented by the two naphthaquinacridines (compare possible dinaphthaquinacridines, Senier and Austin, *Trans.*, 1906, 89, 1387).

The fluorescence exhibited in solution by these compounds is interesting; the quinacridines showing the phenomena in a greater or less degree, as was expected from the presence in their molecules of the acridine fluorophore (compare Meyer, *Zeitsch. physikal. Chem.*, 1897, 24, 468). The ultraviolet waves, when the bases are dissolved in the usual organic solvents, are increased in length, showing blue fluorescence, whilst in solution in glacial acetic acid or in concentrated sulphuric acid, and in one instance in ethyl acetate, the fluorescence is green or even yellowish-green. The fluorescence is especially noteworthy in the instances of 9:10-dimethylpheno- $\frac{N-\beta}{CH-\alpha}$ -naphthaquinacridine

and $\frac{\beta-N-6}{\alpha-CH-5}$ -naphthaquinacridine.

Numerous attempts were made to obtain diquinacridines of other types, but all without success. Thus 6-aminoquinoline (2 mols.) or 6-aminoquinoline (1 mol.) and 8-hydroxyquinoline (1 mol.) were heated in successive experiments with methylene dichloride, methylene di-iodide, and with formaldehyde; again, 6-aminoquinoline (1 mol.) and 8-hydroxyquinoline (1 mol.) were treated with methylene dichloride, methylene di-iodide, and formaldehyde respectively, but the amine alone condensed, and diquinacridine was formed. Similarly, in attempts to prepare a naphthaquinacridine, α -naphthylamine (1 mol.) and 8-hydroxyquinoline (1 mol.) could not be condensed with methylene dichloride; the α -naphthylamine alone reacted, and Senier and Goodwin's dinaphthacridine was obtained. Using benzylidene chloride and benzaldehyde respectively with a mixture of β -naphthylamine and 8-hydroxyquinoline in like manner, only β -N- β - α -CPh- α -dinaphthacridine could be detected.

Several experiments were made with a view to the synthesis of phenoquinacridines, but although some of the results seemed very promising, they have not yet yielded definite compounds. 8-Hydroxyquinoline (1 mol.) was brought together with *m*-4-xylylidine (1 mol.) and *o*-4-xylylidine (1 mol.) respectively, using as condensing agents methylene dichloride, methylene di-iodide, or formaldehyde, and in the same manner, 6-aminoquinoline (1 mol.) with *o*-4-xylylidine or *m*-4-xylylidine.

The 2 : 3 : 7 : 8-tetramethylacridine described was produced from *o*-4-xylylidine (2 mols.) and methylene di-iodide, the former containing an alkyl group in a para-position with respect to its amino-group, which is in accordance with our previous experience (Trans., 1907, 91, 1928).

The work of this inquiry has been unavoidably interrupted, and as some time must elapse before it can be resumed, it is published in its present rather unfinished state.

EXPERIMENTAL.

Condensation of o-4-Xylylidine and o-4-Xylenol with Methylene Dichloride: 2 : 3 : 7 : 8-Tetramethylacridine, $C_6H_2Me_2 \left\langle \begin{array}{c} N \\ | \\ CH \end{array} \right\rangle C_6H_2Me_2$.

o-4-Xylylidine (1 mol.), *o*-4-xylenol (1 mol.), and methylene dichloride (1 mol.) were heated in a closed tube; the temperature was allowed to rise rapidly to 250°, and then slowly to 350°, the higher temperature being maintained for one hour and a-half. After cooling, the contents of the tube were well washed with acetone to which some concentrated solution of ammonium hydroxide was added; by this treatment the base was left in the form of a nearly white powder; this was further purified by washing with methylated spirit, and afterwards with water. The

powder was then either crystallised several times from toluene, or extracted with dilute hydrochloric acid, which yielded the hydrochloride in yellow crystals, from which the base was regenerated by treatment with ammonium hydroxide.

2:3:7:8-Tetramethylacridine crystallises from toluene in clusters of pale yellow, almost colourless, needles, which melt at 273.5° (corr.). It dissolves easily in benzene, ethyl acetate, or toluene, sparingly in acetone, alcohol, or light petroleum. The solution in ethyl acetate exhibits green fluorescence:

0.2567 gave 0.8154 CO_2 and 0.1701 H_2O . C = 86.63; H = 7.36.

0.2357 ,, 12.2 c.c. N_2 (moist) as 11° and 752 mm. N = 6.06.

$\text{C}_{17}\text{H}_{17}\text{N}$ requires C = 86.81; H = 7.23; N = 5.96 per cent.

Aurichloride, $\text{C}_{17}\text{H}_{17}\text{N}, \text{HAuCl}_4$.—This salt was obtained as a yellow precipitate on the addition of a solution of gold chloride to a solution of the base in a mixture of concentrated hydrochloric and glacial acetic acids. The precipitate was collected, washed with dry ether, and dried at 110 — 115° :

0.0740 gave 0.0252 Au. Au = 34.05.

$\text{C}_{17}\text{H}_{18}\text{NCl}_4\text{Au}$ requires Au = 34.26 per cent.

Platinichloride, $(\text{C}_{17}\text{H}_{17}\text{N})_2, \text{H}_2\text{PtCl}_6, 2\text{H}_2\text{O}$.—A solution of platinic chloride was added to a solution of the base in glacial acetic and concentrated hydrochloric acids. The yellow precipitate, which formed at once, was washed with glacial acetic acid, then with ether, and dried at 105° :

0.1347 gave 0.0287 Pt. Pt = 21.30.

$\text{C}_{34}\text{H}_{40}\text{O}_2\text{N}_2\text{Cl}_6\text{Pt}$ requires Pt = 21.29 per cent.

Salicylate.—This salt was prepared, but not analysed. Tetramethylacridine and salicylic acid were brought together in solution in hot toluene. On cooling, the salicylate separated in pale yellow needles, which were purified by recrystallisation from toluene. It is very soluble in benzene, toluene, alcohol, chloroform, or ethyl acetate, less so in acetone, and insoluble in ether or light petroleum.

Condensation of o-4-Xylidine with Methylene Di-iodide:

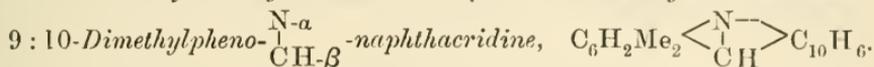
2:3:7:8-Tetramethylacridine.

The same tetramethylacridine as that just described was obtained by this reaction. o-4-Xylidine (2 mols.) and methylene di-iodide (1 mol.) were heated in an open vessel for a few minutes until reaction commenced; the residue was then well mixed, and allowed to cool. The viscous, reddish-brown product was dissolved in alcohol, and the base precipitated from the alcoholic solution by a concentrated solution of ammonium hydroxide. It was collected, washed with water,

dried at 100°, and then crystallised several times from its solution in toluene.

Contrary to previous experience (Senier and Compton, *loc. cit.*), no trace of an intermediate diamine could be detected.

Condensation of o-4-Xylidine and α -Naphthol with Methylene Dichloride:



o-4-Xylidine (1 mol.), *α -naphthol* (1 mol.), and methylene dichloride (1 mol.) were mixed and heated in a closed tube for two hours, the temperature being allowed to rise gradually to 220—230°. After cooling, the deep red, crystalline product was well washed with acetone, and the yellow residue of crude hydrochloride was heated to boiling with alcohol to which a little solution of potassium hydroxide had been added. The free base deposited as the mixture cooled, water was then added, and the base was collected and well washed with water. It was dried first on a porous plate, and afterwards by heating to 100°, and then recrystallised twice from light petroleum.

9:10-Dimethylpheno- $\overset{\text{N-}\alpha}{\underset{\text{CH-}\beta}{\text{C}}}$ -naphthacridine consists of pale dull yellow, thick plates, which melt at 171—172° (corr.). It is very soluble in the usual organic solvents, except alcohol and light petroleum, in which it dissolves sparingly. Its fluorescence in solution is noteworthy, being blue when dissolved in benzene, toluene, alcohol, acetone, ethyl acetate, chloroform, or light petroleum, and green in glacial acetic or concentrated sulphuric acid. It does not show triboluminescence:

0.2115 gave 10.3 c.c. N₂ (moist) at 18° and 769 mm. N = 5.70.

C₁₉H₁₅N requires N = 5.45 per cent.

Platinichloride, (C₁₉H₁₅N)₂.H₂PtCl₆.2H₂O.—This derivative was obtained as a deep yellow, crystalline precipitate when an aqueous solution of platinic chloride was added to a solution of the base in a mixture of glacial acetic and concentrated hydrochloric acids. The precipitate was washed with glacial acetic acid, then with light petroleum, and dried by keeping it for two to three days in a vacuum desiccator:

0.0875 gave 0.0178 Pt. Pt = 20.34.

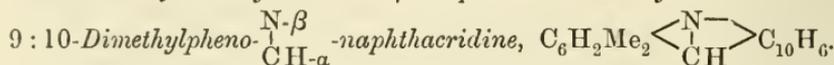
C₃₈H₃₆O₂N₂Cl₆Pt requires Pt = 20.31 per cent.

Aurichloride.—This salt forms a yellow, amorphous powder when precipitated by a solution of gold chloride from a solution of the base in a mixture of glacial acetic and concentrated hydrochloric acids. A specimen was prepared and purified by washing, first with

glacial acetic acid and then with light petroleum. This salt, like the next following, was not analysed.

Salicylate.—The base (1 mol.) and salicylic acid (1 mol.), both in hot benzene solution, were mixed. On cooling, the salicylate separated as an orange-yellow, crystalline powder. It was recrystallised twice from toluene or benzene, when it melted at 99.5° (corr.). It is soluble in benzene, alcohol, light petroleum, toluene, or chloroform.

Condensation of o-4-Xylidine and β -Naphthol with Methylene Dichloride :



A mixture of *o*-4-xylidine (1 mol.), β -naphthol (1 mol.), and methylene dichloride (1 mol.) were heated in a closed tube at a temperature of $260\text{--}270^{\circ}$ for two hours. The contents of the tube after cooling, consisting of a dark red, viscous mass, were thoroughly washed with acetone, and the deep yellow residue was boiled for a few minutes with a mixture of alcohol and a small proportion of potassium hydroxide solution. From the solution thus obtained, the free base was precipitated by the addition of water, and, after several crystallisations from dilute alcohol, was obtained in long pale yellow, almost colourless, glistening needles.

9:10-Dimethyl- $\overset{\text{N-}\beta}{\underset{\text{C-H-}\alpha}{\text{C}}}$ -naphthacridine dissolves readily in benzene, acetone, ethyl acetate, chloroform, glacial acetic acid, or concentrated sulphuric acid, less so in toluene, ether, alcohol, or light petroleum. It exhibits fluorescence—blue, bluish-green, yellowish-green; in benzene, toluene, light petroleum, acetone, ethyl acetate, alcohol, chloroform, or ether it is blue, and the solutions are colourless; in glacial acetic acid it is bluish-green, and the solution is pale yellow; in concentrated sulphuric acid it is yellowish-green, and the solution is deep yellow. The base melts at 187° (corr.):

0.1563 gave 7.7 c.c. N_2 (moist) at 13° and 750 mm. $\text{N} = 5.74$.

$\text{C}_{19}\text{H}_{15}\text{N}$ requires $\text{N} = 5.45$ per cent.

Platinichloride, $(\text{C}_{19}\text{H}_{15}\text{N})_2, \text{H}_2\text{PtCl}_6, 2\text{H}_2\text{O}$.—This was obtained as a yellow precipitate on the addition of a solution of platinic chloride to a solution of the base in a mixture of glacial acetic and concentrated hydrochloric acids. It was washed with light petroleum and dried at 110° :

0.0570 gave 0.0115 Pt. $\text{Pt} = 20.17$.

$\text{C}_{38}\text{H}_{36}\text{O}_2\text{N}_2\text{Cl}_6\text{Pt}$ requires $\text{Pt} = 20.31$ per cent.

Aurichloride, $\text{C}_{19}\text{H}_{15}\text{N}, \text{HAuCl}_4$.—This salt was prepared in the same manner as the platinichloride, using a solution of gold chloride.

The precipitate, which is orange-yellow after washing with light petroleum, was dried at 115°:

0.0849 gave 0.0278 Au. Au = 32.74.

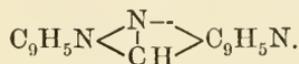
$C_{19}H_{16}NCl_4Au$ requires Au = 32.99 per cent.

Salicylate, $C_{19}H_{15}N, C_7H_6O_3$.—The base and salicylic acid were brought together, both dissolved in hot toluene. From the deep yellow solution which resulted, yellow, glistening prisms deposited on cooling. The compound was recrystallised twice from toluene, washed with toluene, and dried at 110°. It melts at 164° (corr.):

0.1042 gave 3.1 c.c. N_2 (moist) at 21° and 769 mm. N = 3.43.

$C_{26}H_{21}O_3N$ requires N = 3.55 per cent.

Condensation of 6-Aminoquinoline with Methylene Di-iodide or Methylene Dichloride. ^{6-N-6}_{5-CH-5}-Diquinacridine,



6-Aminoquinoline (2 mols.) and methylene dichloride (1 mol.) were heated together in a closed tube for one and a-half hours at 220—230°. The contents were then extracted with methylated spirit, the solution evaporated to dryness, and the black mass resulting was well washed with acetone, containing a little solution of ammonium hydroxide, and then boiled with methylated spirit to which a few drops of solution of potassium hydroxide had been previously added. After cooling, the residue, a dark-coloured powder which contained the acridine, was washed with water, dried at 100°, and the crude base was extracted with toluene. By successive treatment of the resulting reddish-brown, crystalline mass with alcohol containing potassium hydroxide and extraction with toluene, pure crystals were obtained.

By the second method, 6-aminoquinoline (2 mols.) was melted and methylene di-iodide (1 mol.) added. A vigorous action took place in a few minutes, and the mixture solidified. The dark-coloured solid was thoroughly washed with a mixture of acetone and concentrated solution of ammonium hydroxide, dried at 100°, and extracted with toluene. A portion which contained halogen remained insoluble, but was not further examined. The solution in toluene on concentration yielded an orange-yellow, crystalline product. This was collected, and freed from traces of halogen by boiling for a few minutes with methylated spirit to which some solution of potassium hydroxide had been added. The residue remaining, after cooling, was dried at 110°, and crystallised several times from toluene.

^{6-N-6}_{5-CH-5}-Diquinacridine crystallises from dry toluene in clusters

of small needles, which when dried at 110° lose weight and become lighter in colour, due probably to their having contained combined solvent; finally, they become buff-coloured, and melt at 303° (corr.). This compound dissolves easily in benzene, toluene, alcohol, chloroform, nitrobenzene, aniline, glacial acetic acid, or concentrated sulphuric acid; it dissolves less readily in ethyl acetate or acetone; does not dissolve in ether, and is only sparingly soluble in light petroleum. The solution in ethyl acetate is yellow, in other solvents it is colourless. Marked blue fluorescence is shown in solution in concentrated sulphuric acid. The compound does not exhibit triboluminescence.

For analysis the substance was dried at 110° :

0.2388 gave 0.7138 CO_2 and 0.0848 H_2O . C = 81.52; H = 3.94.

0.1899 ,, 24.6 c.c. N_2 (moist) at 13.5° and 748 mm. N = 15.03.

$\text{C}_{19}\text{H}_{11}\text{N}_3$ requires C = 81.14; H = 3.91; N = 14.95 per cent.

Platinichloride.—This salt was obtained as a pale pink precipitate when an aqueous solution of platinic chloride was added to a solution of the base in a mixture of hot glacial acetic and concentrated hydrochloric acids.

Aurichloride.—To the base dissolved in a mixture of glacial acetic and concentrated hydrochloric acids a few drops of solution of gold chloride were added. A yellow precipitate formed, which was washed with dry ether and dried at 105° .

Nitrate, $\text{C}_{19}\text{H}_{11}\text{N}_3 \cdot 2\text{HNO}_3$.—This salt was obtained by dissolving the base in hot dilute nitric acid. After a few hours, pale yellow needles separated. They do not melt, but soften, and darken at 196° (uncorr.):

0.1039 gave 15.6 c.c. N_2 (moist) at 14.5° and 759 mm. N = 17.50.

$\text{C}_{19}\text{H}_{13}\text{O}_6\text{N}_5$ requires N = 17.23 per cent.

Picrate, $\text{C}_{19}\text{H}_{11}\text{N}_3 \cdot (\text{C}_6\text{H}_3\text{O}_7\text{N}_3)_2$.—Hot alcoholic solutions of the base (1 mol.) and of picric acid (2 mols.) were mixed. A yellow precipitate collected, which was washed with alcohol and dry ether and dried at 115° . It is insoluble in light petroleum and toluene, but very slightly soluble in alcohol. It does not melt below 295° , but darkens in colour at 278° :

0.1408 gave 0.2579 CO_2 and 0.0336 H_2O . C = 49.95; H = 2.65.

0.2005 ,, 29.2 c.c. N_2 (moist) at 13° and 755 mm. N = 17.09.

$\text{C}_{31}\text{H}_{17}\text{O}_{14}\text{N}_9$ requires C = 50.30; H = 2.32; N = 17.09 per cent.

Benzoate.—This salt was prepared, but not analysed. It formed readily when hot solutions in toluene of the base and benzoic acid were mixed and kept for some time. Long, pale yellow needles separated, which, after recrystallisation twice from toluene, melted at 180.5° (corr.). It dissolves readily in benzene, toluene, alcohol, or

chloroform; less readily in acetone or ethyl acetate, and is insoluble in ether or light petroleum.

Salicylate, $C_{19}H_{11}N_3(C_7H_6O_3)_2$.—The base (1 mol.) and salicylic acid (2 mols.), both in solution in hot toluene, were mixed, and the mixture kept for some time. A buff-coloured precipitate soon commenced to separate. This was collected and recrystallised several times from toluene. The salt consists of dull yellow needles, which melt at 216° (corr.). It does not exhibit triboluminescence. It is soluble in chloroform, alcohol, ethyl acetate, benzene, toluene, or light petroleum:

0.0922 gave 0.2401 CO_2 and 0.0373 H_2O . C = 71.02; H = 4.49.

0.1770 ,, 11.8 c.c. N_2 (moist) at 17° and 761 mm. N = 7.75.

$C_{33}H_{23}O_6N_3$ requires C = 71.05; H = 4.16; N = 7.55 per cent.

Condensation of 6-Aminoquinoline and α -Naphthol with Methylene

Dichloride or Methylene Di-iodide: α -N-6
 β -CH-5-Naphthaquinacridine,



With methylene dichloride the reaction was brought about in a closed tube. 6-Aminoquinoline (1 mol.) and α -naphthol (1 mol.) were heated for two hours at 240° . The contents of the tube were dissolved by heating to boiling with methylated spirit, and the solution, after concentration, was heated with a concentrated solution of potassium hydroxide. A dull green precipitate resulted, which was dried at 100° and extracted with boiling light petroleum. The solution on cooling deposited the base as a yellow, crystalline powder. This was crystallised twice from ethyl acetate.

When methylene di-iodide was employed, the operation was conducted in an open vessel. The same proportions as before were used. The base and the α -naphthol were melted together and heated to 120° , and the methylene di-iodide was added to the mixture. The heating was continued until a temperature of 130° was attained, when the reaction commenced and the source of heat was removed until it moderated. Afterwards, heat was again applied, and the temperature was kept at 170° for fifteen minutes. On cooling, the dark solid was dissolved by heating to boiling with alcohol to which a little potassium hydroxide had been added. An inky solution was obtained, to which, when cool, a small proportion of water was added, which precipitated a dark powder. This was collected, dried, and extracted with hot light petroleum, from which solution, on cooling, a yellow, amorphous powder separated. From this powder the pure base was obtained by recrystallising twice from ethyl acetate.

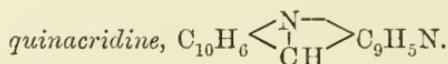
α -N-6
 β -CH-5-Naphthaquinacridine crystallises in small, pale yellow needles, which melt at 268—268.5° (corr.). It dissolves readily in benzene, toluene, nitrobenzene, aniline, chloroform, glacial acetic acid, or concentrated sulphuric acid, less readily in acetone, light petroleum, ethyl acetate, or alcohol, and is insoluble in ether. The solutions are faintly fluorescent: blue in most solvents, but green in glacial acetic acid and concentrated sulphuric acid:

0.1846 gave 15.9 c.c. N₂ (moist) at 18° and 760 mm. N = 9.95.

C₂₀H₁₂N₂ requires N = 10.00 per cent.

Aurichloride.—This salt was prepared, but not analysed. It consists of an orange-yellow precipitate, obtained by adding a solution of gold chloride to a solution of the base in a mixture of glacial acetic and concentrated hydrochloric acids. The precipitate was washed, first with glacial acetic acid, and then with light petroleum.

Condensation of 6-Aminoquinoline and β -Naphthol with Methylene Dichloride, Methylene Di-iodide, or Formaldehyde: β -N-6
 α -CH-5-Naphtha-



Although numerous experiments were made by each of the three methods, we were not able to obtain this compound in a sufficiently pure state to give a constant melting point or a satisfactory analysis.

When methylene dichloride was used, the reaction was brought about in a closed tube heated to 215° for two and a-half hours. With methylene di-iodide, an open vessel was employed, in which 6-aminoquinoline and β -naphthol were melted, and the methylene di-iodide added. In this case the action was at first violent, and had to be moderated by cooling, but afterwards the temperature was increased to 140°. With formaldehyde (trioxymethylene), the method was similar to the last. The products by each method were treated in the usual way to isolate the base. In all cases, crystals, yellow prisms, were obtained from light petroleum, benzene, or toluene, which melted about 220°. The compound dissolves very easily in most organic solvents, less so in light petroleum or ether. It shows marked fluorescence, which is blue in most solvents, but green in either glacial acetic or sulphuric acid:

0.1269 gave 0.3963 CO₂ and 0.0502 H₂O. C = 85.17; H = 4.39.

0.1948 ,, 17.2 c.c. N₂ (moist) at 16° and 763 mm. N = 10.33.

0.2538 ,, 20.8 c.c. N₂ (moist) ,, 16° ,, 762 mm. N = 9.78.

C₂₀H₁₂N₂ requires C = 85.71; H = 4.28; N = 10.00 per cent.

Salicylate, $C_{20}H_{12}N_2C_7H_6O_3$.—The base (1 mol.) and salicylic acid (1 mol.), each dissolved in hot toluene, were mixed, and the mixture allowed to cool, when a yellow, crystalline powder quickly separated. After twice recrystallising from toluene, it melts at 198° (corr.). The salt dissolves in benzene, toluene, alcohol, acetone, ethyl acetate, or chloroform, but does not dissolve in ether or light petroleum. Blue fluorescence is observed in the solutions in alcohol, ethyl acetate, acetone, or chloroform. The solutions in benzene and toluene are not fluorescent:

0.0656 gave 3.9 c.c. N_2 (moist) at 16° and 764 mm. $N = 6.96$.

$C_{27}H_{18}O_3N_2$ requires $N = 6.70$ per cent.

UNIVERSITY COLLEGE,
GALWAY.

CLXXXIV.—*The Atomic Weight of Chlorine.*

By ROBERT WHYTLAW GRAY and FRANK PLAYFAIR BURT.

THE results of recent researches on the atomic weight of chlorine furnish a good illustration of the uncertainties inherent in all atomic weight determinations. The values obtained in any one investigation agree closely among themselves, and vary regularly about a mean. The mean values from different methods of experiment, however, are often much more divergent than the errors of measurement would lead one to expect. The following table exemplifies these statements, and shows clearly that some of the values are affected by small constant errors:

Atomic Weight of Chlorine. O = 16.

Obtained by	Ratio measured.	H = 1.0076.	H = 1.00787.	Probable error.
Dixon and Edgar ¹	H:Cl	35.463	35.471	∓ 0.0019
Edgar ²	Cl:H and Cl:HCl	$\left\{ \begin{array}{l} 35.462 \\ 35.461 \end{array} \right.$	$\left\{ \begin{array}{l} 35.470 \\ 35.469 \end{array} \right.$	± 0.0008 —
Noyes and Weber ³	H:Cl and H:HCl	35.452	35.461	∓ 0.0008
Richards ⁴	$AgCl:Ag, NH_4Cl:AgCl,$ and $AgNO_3:Ag$	35.457	35.456	very small
Guye and Fluss ⁵	Cl:O	35.466	—	—
„ „ Ter-Gazarian ⁶	Density of HCl and critical constants ...	35.461	35.461	—

¹ *Phil. Trans.*, 1905, **205**, 169.

² *Phil. Trans.*, 1908, *A*, **209**, 1.

³ *J. Amer. Chem. Soc.*, 1908, **30**, 13.

⁴ *J. Amer. Chem. Soc.*, 1909, **31**, 6.

⁵ *J. Chim. phys.*, 1908, **6**, 795.

⁶ *Compt. rend.*, 1906, **143**, 1233.

Since the atomic weight of chlorine is one of the fundamental values on which the atomic weights of a large number of the

elements depend, it is of great importance that it should be known with a high degree of precision. A careful examination of the results of recent investigations by Brauner (Abegg's *Handbuch*, II., i. 185) has led him to the conclusion that 35.458 is to be regarded as the most probable value, yet from the figures just quoted it seems by no means certain that the higher value 35.470 may not, after all, be a nearer approximation to the truth. In order to obtain further evidence, we have studied the question from a physico-chemical standpoint, and the present research contains an account of the determination of this constant by methods which are essentially different from those employed either by Dixon and Edgar, Noyes and Weber, Richards and his colleagues, or by Guye and Fluss. The work consists of a detailed study of hydrogen chloride, and falls into three parts, which comprise:

1. A revision of the density of the gas.
2. Its volumetric analysis.
3. A determination of the form of the pv isothermal at 0° , between the pressure limits 780 and 150 mm.

PART I.—*The Density of Hydrogen Chloride.*

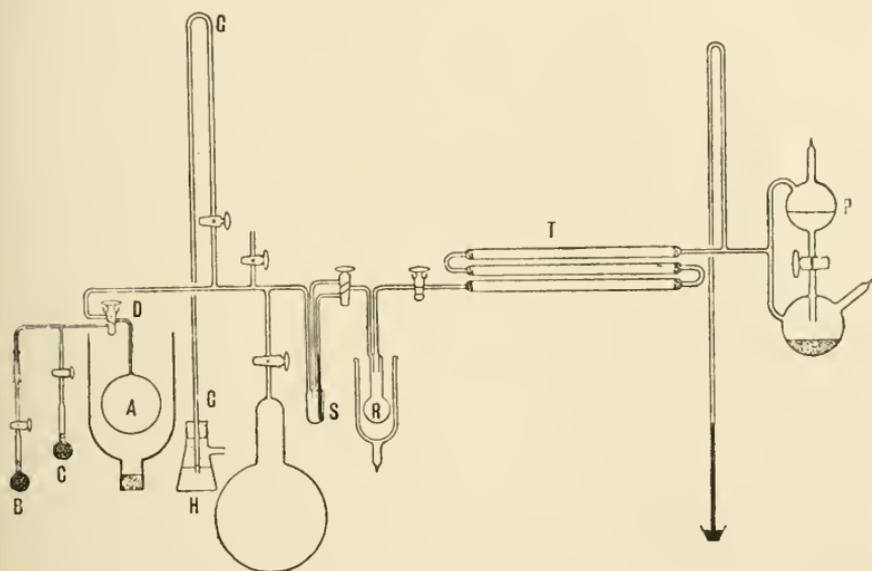
Comparatively few determinations of the density of this gas have been made. Leduc (*Ann. Chim. Phys.*, 1898, [vii], 15, 1) deduced from his experiments the value 1.6407 grams for the weight of a normal litre of the gas. Later, Guye and Ter-Gazarian (*Compt. rend.*, 1906, 143, 1233) obtained from four determinations the mean result 1.6398, which agrees well with the value 1.6397 resulting from six experiments carried out by one of us a few months later (*Proc.*, 1907, 23, 119). For reasons which will be given subsequently, we consider the latter value distinctly too large.

In our experiments the gas was weighed after it had been condensed on cocoanut charcoal. The weighing bulb had a capacity of about 20 c.c. The bulbs in which the volume of the gas was measured had a capacity of about 450 c.c. One bulb was made of soda-glass, and the other of transparent, vitreous silica. The latter was attached to the rest of the apparatus by means of a capillary glass-silica connexion, the two portions of the connexion being cemented together with paraffin wax. The bulb and connexion were made by Messrs. Johnson and Matthey for this research.

The method in all particulars is the same as that previously used by one of us for the determination of the density of nitric oxide (Gray, *Inaug. Diss.*, Bonn, 1907, "Ueber das Atomgewicht des Stickstoffs"). The details are best followed from Fig. 1. A is the volume-bulb, which could be put in connexion either with

the vessels used for storing and purifying the gas or with the charcoal absorption bulb *B*. The gas in *A* was kept at 0° by means of a bath of ice and distilled water. *A* was filled to a pressure slightly above atmospheric, and the excess of gas was allowed to escape through the sulphuric acid gauge *GG*. Complete adjustment of the gas pressure was effected by lowering the flask *H*; the standard barometer was then read, and the stopcock *D* turned off. The transference of the measured volume of gas from *A* to the weighed absorption bulb *B* was brought about by slowly cooling *B* by means of liquid air, and by opening the taps *D* and *E*. Before this operation was commenced, it was necessary to free

FIG. 1.



the capillary connexion tubes from air. This was accomplished by a ten minutes' immersion of the second charcoal-bulb *C* in liquid air. At the conclusion of an experiment, the absorption bulb *B* was detached, cleaned, and suspended from the balance-beam, and weighed after an interval of an hour. Meanwhile the empty bulb *A* was refilled, and the cycle of operations repeated. After two experiments, the absorption bulb *B* was heated, and the condensed gas removed by means of a filter-pump. After 900 c.c. of gas had been absorbed by the charcoal, the pressure inside bulb *B* did not exceed a few cm. of mercury at room temperature, so that an even larger volume of hydrogen chloride could obviously have been condensed and weighed in the 20 c.c. bulb.

With regard to the actual measurements little need be said. As can be seen from the following data, the volumes of the two bulbs were easily determined with a high degree of accuracy by weighing them full of boiled distilled water in the usual way. The bulbs were filled with water at 0°, and weighed at room temperature. A small glass bulb temporarily sealed on to the capillary stem provided space for the expansion of the water as the temperature rose from 0° to that of the balance case. A set of weights ranging from 1 kilogram to 1 milligram was used throughout the research, and their relative values were ascertained by Richards' method (*Zeitsch. physikal. Chem.*, 1900, **33**, 605).

We did not require to know the absolute values of the weights, since they only served to counterpoise water and gas filling the bulb under measured conditions. The effect on the density bulb of a variation in the buoyancy of the air was eliminated in the usual way by employing a counterpoise. In calculating our results, all weighings were corrected for the deviation of the face values of the weights from their true relative values in air, and also for the air displacement of the weights. In calculating the density results which we announced in a previous note (*Proc.*, 1908, **24**, 215), we made the perhaps not unnatural mistake of assuming that a correction was necessary for the difference between the air-displacement of platinum and brass, an assumption which would have been logical if the original calibration had been carried out in a vacuum. We overlooked the fact that this adjustment was made automatically when the weights were compared with each other in air, and that consequently the same correction for air-displacement must be made for both metals. This mistake appreciably alters our final density, and we take this opportunity of pointing out the existence of an error in the values already published.

Volumes of the Bulbs at 0°, all corrections made.

	Glass bulb.		Silica bulb.
I.	465·857 c.c.	457·419 c.c.
II. After a three months' interval.....	465·855 ,,	After heating to redness.....	457·422 ,,

The charcoal absorption bulb *B* was weighed on a long-beam Oertling balance, and the probable error of weighing was not greater than 0·03 milligram. It was counterpoised in the usual way by a bulb of nearly the same capacity, surface, and mass. On account of the small volume of this bulb, and the small variation in internal pressure due to the absorbed gas, the correction for change in buoyancy on exhaustion was of a negligible order. The

height of the mercury column of the standard barometer was referred to a glass scale, and read by means of a telescope and micrometer eye-piece to 0.03 mm. The temperature of the barometer column could be measured to within 0.2°. The absolute distance between two fixed points on the glass scale was ascertained for us at the Standards office through the kindness of Major Macmahon. A second scale used in some of the measurements was compared with an "invar" meter recently recalibrated at the National Physical Laboratory. For the loan of this standard, and for the use of the necessary reading instruments, we desire to thank Professor Trouton and Mr. Eumorphopoulos, of University College.

The Preparation of Pure Hydrogen Chloride.

The gas was prepared in three ways:

1. From sulphuric acid and sodium chloride.
2. From sulphuric acid and ammonium chloride.
3. From silicon tetrachloride and water.

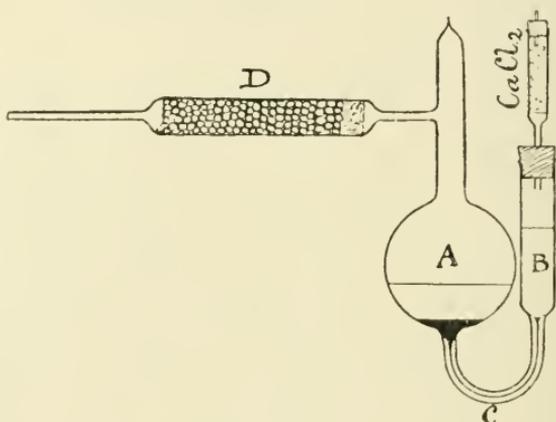
The sulphuric acid was prepared by the contact process, and proved to be very pure. The sodium chloride was prepared by precipitating from its aqueous solution, by means of gaseous hydrogen chloride, a very pure sample of the salt obtained from Messrs. Hopkin and Williams. The sodium chloride was subsequently recrystallised twice from water, and a careful examination failed to detect traces of other halogens. The ammonium chloride was purified after the method of Stas (*Œuvres complètes*, **1**, 373). The salt was recrystallised twice from water, and the separation of the mother liquor was facilitated by the use of a centrifugal machine. The silicon chloride was obtained from Kahlbaum, and contained no free chlorine and no bromine compounds.

The interaction of the concentrated sulphuric acid and sodium or ammonium chloride was carried out in a high vacuum in a sealed glass vessel, *P*, of the form shown in Fig. 1 (Guye and Bogdan, *J. Chim. Phys.*, 1905, **3**, 537). The salt was introduced into the lower, and the acid into the upper bulb, and the neck sealed off with a mouth blowpipe before exhaustion. The gas was dried by passage over phosphoric oxide contained in the tubes *T* in the diagram, and was then condensed to a solid in the vessel *R*. From *R* the hydrogen chloride was boiled off and condensed in the second fractionating vessel *S*; when the latter was about half full, the tap was reversed, and the gas allowed to bubble through its own liquid. In this way any impurities possessing a higher boiling point than hydrogen chloride were partly or wholly eliminated. That fraction of the gas which passed over at an early stage of the operation was judged to be the purest, and was stored for later

use in two large 5-litre bulbs, which had been previously evacuated, first by means of a Fleuss pump, and finally by means of charcoal cooled in liquid air. The impure gas was then allowed to evaporate, and the connecting tubes and fractionating vessels were freed from this residue with a Töpler pump. Before filling the density bulb, the gas was condensed out of the storage bulbs and put through another series of fractionations. As a rule, the first fraction was returned to the storage bulb in case it might contain traces of air which had been entangled or dissolved in the solid hydrogen chloride and thus escaped removal by the pump.

The preparation of the gas from silicon tetrachloride necessitated a different form of generator (Fig. 2). The distilling flask *A* was partly filled with distilled water. The silicon tetrachloride was

FIG. 2.



introduced into the cylinder *B*, which was protected by a calcium chloride tube from the entrance of moisture. *A* and *B* were connected by means of a tube *C*, which, before the introduction of water into *A*, had been filled with dry mercury. During an experiment the apparatus was immersed in a freezing-bath in order to moderate the reaction. By slightly reducing the pressure in *A*, a small quantity of silicon tetrachloride was sucked over, and the reaction started. The mixture of air and hydrogen chloride was passed through a tube *D*, packed with moistened glass beads, and then condensed in a large fractionating vessel. The air was pumped off through the Töpler pump, and the hydrogen chloride carefully fractionated in order to eliminate the last traces of the silicon tetrachloride.

Impurities in the Gas.

Two sources of contamination were discovered in the early stages of the investigation. The gas was found to react with the phosphoric oxide, forming a volatile phosphorus compound, which was decomposed by the mercury of the Töpler pump, a solid yellowish film being deposited on the glass surfaces. The production of this compound has already been observed by Richards. When the gas issuing from the phosphoric oxide tubes was led into water, the solution gave a yellow precipitate with nitric acid and aqueous ammonium molybdate. By employing phosphoric oxide distilled in a stream of oxygen, the formation of this compound was lessened. It was found, however, that the gas could be freed from this impurity by two distillations carried out in the manner described; after this treatment, the concentrated aqueous solution of hydrogen chloride contained no detectable quantity of phosphorus.

The action of the gas on the rubber-vaseline lubricant initially used for the glass stopcocks proved another source of contamination. The grease was rapidly charred, and the taps soon ceased to maintain a vacuum. At the same time, organic compounds volatile in the gas were formed, and the density of the latter increased. The substitution of metaphosphoric acid for the grease was considered, but abandoned on account of the large volume of hydrogen chloride it is capable of absorbing (Baker, *Trans.*, 1898, **73**, 422; Gutmann, *Annalen*, 1898, **229**, 3). Finally, a lubricant, consisting solely of pure paraffins, was prepared, and this proved to be without action on the gas and to be capable of rendering a carefully-ground stopcock gastight for an indefinite period.

After the gas had been kept for some time in the storage bulbs, it was found to contain traces of chlorine, and to cause phosphoric oxide to deliquesce. This was doubtless due to chemical action between the hydrogen chloride and traces of air adsorbed on the glass surfaces of the apparatus, or given off slowly from the tap-grease (Berthelot, *Compt. rend.*, 1897, **125**, 746). To eliminate the chlorine, the gas was passed over clean mercury before liquefaction (Shenstone, *Trans.*, 1897, **71**, 485). Any mercury vapour carried by the gas was, of course, condensed in the fractionating vessels, and could not find its way into the density bulb.

The crude gas from the ammonium and sodium chlorides and sulphuric acid certainly contained other impurities. The last fraction of the liquefied gas nearly always held in suspension a slight white precipitate, which volatilised less readily than the

hydrogen chloride itself. On examination of the gas resulting from the precipitate, hydrogen sulphide was discovered. Its presence was evident from the odour of the aqueous solution of the gas, and also from the formation of methylene-blue in a solution of *p*-aminodimethylaniline sulphate. The mode of its origin is, however, obscure. It is certain that neither the ammonium nor sodium chlorides nor the sulphuric acid contained sulphides, and one can only suppose that it originated from the reduction of the sulphuric acid itself during the evolution of the gas. The complete elimination of traces of hydrogen sulphide from hydrogen chloride is not easy. It might be supposed that it would be removed by mercury, but mercury does not attack perfectly dry hydrogen sulphide. Again, it might react with traces of chlorine, but in view of the absence of moisture this is also doubtful, and, moreover, chlorine was not always present. For its elimination we had to rely entirely on the fractional distillation of the liquefied gas.

With regard to the gas obtained from silicon tetrachloride and water, it is difficult to see how it could have contained any foreign gases besides a possible trace of chlorine and vapour of the tetrachloride. It was certainly purer initially than the product from the other two reactions. After the final fractionations, however, the gas from all three sources was certainly very pure. When condensed, the liquid was perfectly clear and colourless, and left no residue on evaporation. On further cooling, the liquid yielded a pure white, crystalline solid, which melted sharply at a constant and definite pressure of 100 mm. The gas was entirely free from air, for a little boiled water or a small piece of solid potassium hydroxide absorbed it completely. It contained no compound of phosphorus, and chlorine was entirely absent. The only likely impurity, in the case of gas prepared by the action of sulphuric acid on a chloride, was hydrogen sulphide. For reasons which will be given later, we are convinced that it could not have been present in sufficient quantity to influence the density results.

We noticed a curious phenomenon connected with the condensation of hydrogen chloride, which is worthy of mention. When the solidified gas was sublimed, or when the gas itself was slowly condensed at the temperature of liquid air, the crystalline product almost always exhibited a rose-pink coloration in patches. On allowing the solid to become warm, the pink colour entirely vanished before the melting point was reached. We have been unable to concentrate the coloration by either fractional distillation or sublimation of the hydrogen chloride. On the supposition that it is produced by a small trace of some highly coloured impurity, we have tried to increase its amount by adding small quantities of

other gases and vapours, for example, chlorine, iodine, bromine, nitrogen peroxide, sulphur dioxide, and hydrogen sulphide, to hydrogen chloride and condensing the mixture, but in no instance was there any visible increase of the coloration. The phosphoric oxide was not responsible for its production, for in one set of experiments sulphuric acid only was used as a desiccating agent, but the pink colour still made its appearance. It is noteworthy that Inglis (*J. Soc. Chem. Ind.*, 1906, **25**, 152) obtained a gas condensing to a red solid from the lead chamber gases of a sulphuric acid plant. The presence of a trace of moisture prevents the appearance of the colour, for we were never able to obtain it unless the gas had been previously very carefully dried. The intensity of the coloration varied in different specimens, but it did not appear to influence in any way either the density of the gas or its volumetric composition. We have, therefore, concluded that if the pink colour denotes the presence of an impurity, the latter must have been present in extremely small amount.

Adsorption of Hydrogen Chloride on Glass Surfaces.

In a research of this nature, the adsorption of the gas on the internal surface of the density bulb calls for careful consideration. We have confirmed the observation of Guye (*Compt. rend.*, 1906, **143**, 1233), that the density of the gas in a new bulb decreases with each filling, and finally reaches a minimum value which varies fairly regularly about a mean. In all probability this decrease is due to the presence on the surface of the bulb of a film of moisture which absorbs the gas in relatively large quantities; this film being partly absorbed by the charcoal in the weighing bulb, together with the gas itself, the apparent density is too great. With each successive filling the film should diminish, and the density reach a constant value. As a matter of fact, in our method of working, a limit of desiccation was certainly reached after the first few fillings, and since, throughout the whole series of experiments in the same bulb, there was never any necessity for removing the stopcock, any source of error due to the moisture film either vanished or remained at a minimum. In the absence of all avoidable moisture there was, however, a small but appreciable amount of gas adsorbed by the glass.

These conclusions are supported by the following experiments. A glass cylinder, fitted with a stopcock at either end, was connected with an adjustable mercury reservoir, and completely filled with dry mercury. On opening the upper tap, carefully dried hydrogen chloride entered and displaced the mercury; the gas

itself was then completely displaced by raising the mercury reservoir, and the upper tap was closed. On lowering the reservoir again, a vacuum was produced, and the mercury was drawn down until the meniscus fell below the lower tap. It was observed that during this operation small bubbles of gas came off from the walls of the vessel and collected in the cylinder. On taking special precautions beforehand to exclude moisture, the quantity of gas evolved in this way was visibly less. In order to make the experiment more definite, the cylinder was detached from the rubber tube connecting it with the mercury reservoir, and about 1 c.c. of a *N*/50-silver nitrate solution, acidified with a little dilute nitric acid, allowed to enter. Care was taken to avoid the presence of small mercury globules in the cylinder and tubes leading to the taps. When the cylinder had been carefully dried by a stream of pure air passed over phosphoric oxide, only a faint opalescence was produced, but the presence of a very small amount of moisture was sufficient to cause a marked turbidity in the reagent. Hence one may conclude that adsorption of the gas by well-dried glass surfaces is very small. That even this small amount of gas is taken up by cooled cocoanut charcoal is certain from the fact that on letting a little of the silver nitrate solution into the exhausted volume bulb of our apparatus at the end of each series of determinations, no trace of opalescence was ever observed. This test was fairly delicate, for blank experiments carried out with the same volume of silver nitrate solution showed that as little as 2 cub. mm. of the gas could be readily detected.

This last test also negatives the supposition that the glass was decomposed to any appreciable extent by the hydrogen chloride; had this been the case, chlorides of the bases present would have been formed and have yielded a precipitate with aqueous silver nitrate.

From the foregoing experiments, it is clear that a rigorous desiccation of the density bulb was essential if good results were to be obtained. A silica bulb was used in the later determinations, for it was very much easier to dry its interior completely. The silica bulb was heated to redness and repeatedly filled with dry air and exhausted before attaching it to the apparatus.

In our earlier density measurements, when rubber-vaseline grease was used as a tap-lubricant, it was only possible to make a small number of experiments without regreasing the bulb stopcock, and this involved the admission of moisture. For this reason, and also on account of the contamination of the gas by the grease, we consider these results untrustworthy, and they are not recorded in the final table.

In some experiments, which will be described later, we have measured the volume of gas removable from the glass surfaces in a vacuum. The method was similar to that employed in the qualitative experiments just described, but care was taken to displace the gas by the mercury at constant pressure. The bulb was made of the same glass as that used for the densities, and was kept at 0° throughout the operation. The amount of gas given off from each square cm. of surface amounted to 0.1235 cub. mm., and this quantity was constant at constant temperature and for any given initial pressure. On the assumption that this adsorbed gas exerted no pressure, we have made use of these results to correct our densities. The surface of the density bulb being 291 sq. cm., the volume of gas adsorbed by it was 0.036 c.c., and its weight 0.00006 gram, and hence the amount to be subtracted from the weight of a litre of the gas was 0.00013 gram. This correction only applied to the glass bulb, and since no direct experiments on adsorption on silica surfaces have been made, we have introduced no alteration in the measurements carried out in the silica bulb.

Another possible source of error was the solution of traces of hydrogen chloride in the grease used for the stopcocks. An attempt was made to measure this. It was found that the amount of gas dissolved by the grease on the bulb stopcock did not exceed 0.01 c.c., and since this amount of gas represents an error smaller than the mean probable error in any of the series, we have decided to neglect it.

In the following table we have applied to the numbers in the third column a small correction for the slight deviation of hydrogen chloride from Boyle's law between 760 mm. and the observed barometric height.

TABLE OF RESULTS.

Series I.

Glass bulb. Volume at 0° = 465.856 c.c. Gas from sodium chloride and sulphuric acid.

	Weight of gas condensed on charcoal : all corrections made.	Barometric pressure at 0° : London : all corrections made.	Weight of 1 litre of gas at 0° and 760 mm. in London, corrected for compressibility of HCl.
1.	0.76097 gram	756.76 mm.	1.64053 grams
2.	0.75731 "	753.38 "	1.64004 "
3.	0.75481 "	750.83 "	1.64020 "
4.	0.75968 "	755.79 "	1.63986 "
		Mean.....	1.64016 grams ±0.00010

Series II.

Glass bulb. Gas from silicon tetrachloride and water.

	Weight of gas condensed on charcoal: all corrections made.	Barometric pressure at 0°: London: all corrections made.	Weight of 1 litre of gas at 0° and 760 mm. in London, corrected for compressibility of HCl.
1.	0.75841 gram	754.38 mm.	1.64022 grams
2.	0.75959 "	755.65 "	1.63999 "
3.	0.76169 "	757.83 "	1.63976 "
4.	0.76150 "	757.15 "	1.64083 "
5.	0.75922 "	755.14 "	1.64030 "
6.	0.76186 "	757.79 "	1.64021 "
7.	0.76194 "	757.84 "	1.64027 "
		Mean.....	1.64023 grams \mp 0.00008

Series III.

Quartz bulb. Volume at 0°=457.420 c.c. Gas from ammonium chloride and sulphuric acid.

1.	0.74622 gram	756.26 mm.	1.63950 grams
2.	0.74643 "	756.18 "	1.64013 "
3.	0.75295 "	762.87 "	1.63984 "
4.	0.75776 "	767.31 "	1.64069 "
5.	0.75762 "	767.35 "	1.64031 "
6.	0.75216 "	761.93 "	1.64017 "
7.	0.73831 "	747.85 "	1.64050 "
8.	0.73646 "	745.99 "	1.64051 "
9.	0.74316 "	752.99 "	1.63992 "
10.	0.75651 "	766.37 "	1.64001 "
		Mean.....	1.64016 grams \mp 0.00008

From the means of Series I and II, there has to be subtracted 0.00013 gram, which represents the weight of adsorbed gas given off from the walls of the glass bulb. Then the means of the three series become:

Series I	1.64003
, II	1.64010
,, III (unaltered)	1.64016

The final mean calculated by the method of least squares is 1.64011 \mp 0.00005, and the weight of a normal litre of gas (namely, the weight of 1 litre at 0° and 760 mm., Lat. 45°) is:

$$\frac{1.64011}{1.000588} = 1.63915 \text{ gram,}$$

where 1.000588 is the factor which expresses the difference in the value of "g" between London and Lat. 45°.

On comparing the individual values in any one series, it will be seen that the maximum divergence is very much greater than the probable errors of measurement. We must say that in view of

the concordance of the results obtained by the same method with nitric oxide, a closer agreement was expected. It hardly seems likely that the discrepancies can be entirely explained by the presence of impurities in the gas, and our work on the analysis of hydrogen chloride supports this view. Moreover, in neither series is there any progressive change in weight, although the densities correspond with successive fractions of the liquefied gas. On the other hand, the agreement between the mean values of the three series leaves nothing to be desired, and in consequence of the large number of determinations, we think that our final figure is an accurate approximation to the true density of hydrogen chloride.

PART II.—*The Volumetric Analysis of Hydrogen Chloride.*

In order to deduce the molecular weight of hydrogen chloride from the value obtained for the density, it was possible to adopt several modes of procedure, involving the knowledge of either the exact volume of hydrogen yielded by two volumes of the gas, or of the relative compressibilities of hydrogen chloride and some standard gas, such as oxygen. A third method was to determine and reduce the critical constants of the gas according to the method worked out by Guye (*J. Chim. Phys.*, 1908, **6**, 795). These two latter methods involve a somewhat uncertain extrapolation, which is not the case in the first method, and for this reason we thought the most satisfactory course was first to measure accurately the volumetric composition of the gas.

On account of the deviation of hydrogen and hydrogen chloride from the gas laws, it is clear that the ratio of the densities at 0° and 760 mm. does not accurately represent the ratio of the molecular weights. If, however, the volumes occupied by chemically equivalent quantities of the two gases are known, the required ratio can at once be deduced.

The actual course of procedure was to find the volume of hydrogen obtainable from exactly two volumes of hydrogen chloride, both gases being measured in the same apparatus at 0° and 760 mm., that is, the same temperature and pressure at which the density measurements were made. In essentials the method was as follows. The two volumes of hydrogen chloride were measured successively in a constant pressure pipette, which, together with the mercury manometer column, was immersed in melting ice throughout the determination. After each filling the gas was collected in a bulb, and there decomposed by means of heated aluminium. The hydrogen produced was then returned to the measuring vessel, and since its volume was a little greater than

half the total volume of the hydrogen chloride, it was necessary to increase the volume of the pipette slightly in order to recover the original pressure. The accurate measurement of this small volume increment supplied the data for determining the ratio of chemically equivalent volumes of hydrogen and hydrogen chloride.

The constant pressure pipette consisted essentially of the thick-walled bulb *A* (Fig. 3) of about 300 c.c. capacity, connected below by means of a short length of capillary tubing with the dead-space *B*, and above with another capillary tube carrying a two-way stopcock *C*. The dead-space was furnished with a glass point. The upper chamber of the manometer also carried a glass point, and communicated with the lower chamber containing the dead-space as shown in the figure. The distance between the two points was maintained constant by means of a stout glass rod *W*, sealed at its upper end to the manometer head, and at its lower to the capillary tube connecting the pipette with the two-way tap *C*. For our purpose, it was not necessary to know the exact distance between the two points. It was, however, essential that this length should not differ much from 760 mm. In sealing together the two ends of the glass rod when the apparatus was being set up, special care was taken to ensure the correct adjustment of the two points, and subsequent measurement with a cathetometer proved the final distance between them to be within 0.1 mm. of the required length. It was further necessary to guard against any alteration of the vertical distance between the two points during an experiment. The whole apparatus was rigidly fixed to a heavy iron bar with a tripod base, and any vertical displacement could at once be detected by the plumb-line *VV*. By levelling the tripod it was easy to reset the plumb line, and in practice this could be done without putting any dangerous strain on the sealed glass connexions. We adopted the method of Rayleigh (*Proc. Roy. Soc.*, 1893, 53, 137) to ensure the absence of air or moisture in the manometer head. The vacuum in the latter was verified from time to time by means of a Töpler pump (not shown in figure), and a small tube containing phosphoric oxide served to retain traces of water vapour.

Sealed to the capillary between the bulb and the tap *C* was a capillary T-piece expanding into a tube of a few c.c. capacity, which terminated at its lower end in another capillary carrying a tap *S*. During the measurement of the hydrogen chloride, this side-tube, which we have called the volume-adjuster, was filled with mercury up to the top. It only came into use during the measurement of the hydrogen, and enabled the necessary increase in volume to be made.

As can be seen in the diagram, the pipette, manometer column,

on account of the difficulty of seeing the point. To obviate this, we surrounded the dead-space by a small subsidiary bath *U*, which could be filled with a suitable liquid cooled below 0° by means of the funnel. For this purpose we used brine, and we found no difficulty in keeping the temperature within one degree of zero when the final setting was made. On account of the small volume of the dead-space (almost exactly 1 c.c.), a variation of this order did not affect the results. The mercury required for displacing gas from the pipette was contained in a reservoir *D*. An air-catch *T* guarded the pipette from any trace of leakage at the rubber junction.

Calibration of the Pipette.—The pipette was calibrated from the tap *C* to the glass point in the dead-space by means of mercury after the apparatus had been set up, and before the side-tube leading to the manometer head had been sealed on. For this purpose a stopcock on capillary tubing, which was drawn out to a fine point, was temporarily fused on to the glass tubing below the dead-space. The pipette was then filled with mercury and cooled to 0° . The whole volume of mercury from the tap *C* was run out and weighed. Mercury was introduced again until the meniscus was set to the glass point, and this quantity was then run out and weighed. In a second calibration, the required volume was obtained directly by weighing the mercury run out from the tap to the dead-space point. During the calibration, the tubing below the dead-space was wrapped in cotton-wool to prevent the temperature from changing. The actual temperature in this part of the apparatus was not of importance so long as it remained approximately constant. The initial and final temperatures recorded by a thermometer in the cotton-wool were found not to vary by more than a degree throughout the operation, a difference involving no correction on the total volume.

The mercury was weighed in four portions, and a set of platinised brass weights, ranging from 1 kilogram downwards, which had been carefully compared with each other, were used for this purpose. The same set of weights was employed for weighing the mercury withdrawn from the volume-adjuster in the measurement of the hydrogen during the analyses. In this way the volume increment was compared very exactly with the total volume of the gas, and the accurate evaluation of this ratio was all we desired to accomplish. The absolute volumes of the mercury withdrawn could have been calculated by making the usual corrections for air-displacement, and by comparing our weights with a standard set, but this was unnecessary, for in no circumstances could the required ratio have been appreciably altered by changes in atmospheric conditions during weighing.

Calibration Values.

		Temp. of cotton wool.
I. Weight of mercury from tap <i>C</i>	4365.749 grams	2.5°
" " " dead-space point	193.968 "	2.9
" " " filling pipette from tap		
<i>C</i> to point.....	4171.781 "	—
Volume	306.850 c.c.	—
II. Weight of mercury from tap <i>C</i> to dead- space point	4171.750 grams	1.2—2.3
Volume	306.848 c.c.	—
Mean	306.849 c.c.	—

Introduction and Measurement of the Gas.

The purified gas was distilled into the pipette through the taps *K* and *C** until the points in *B* and *E* were approximately set. The tap *K* was then closed, and the final setting effected by means of the pressure-adjuster *G*; this requires no special description. By arranging the small reservoir *H* at a suitable height, and swinging the tap *J*, minute quantities of gas could be introduced into or withdrawn from the pipette. By the alternate manipulation of the pressure-adjuster and of the screw controlling a wooden clip, which compressed the rubber tubing connecting the reservoir *D* to the pipette, the two mercury menisci were set to their respective points. As Lord Rayleigh has shown, this method enables a very accurate adjustment to be made (*Phil. Trans.*, 1902, *A*, 198, 418).

With regard to temperature, the only parts of the system not actually surrounded by melting ice were the dead-space, which was cooled in a brine-bath as described, the short piece of capillary tubing connecting the dead-space and pipette, and the short column of mercury in the manometer from *L* to *M*. On account of a slow leaking of cold water from the bath above, the temperature of these portions of the apparatus was reduced nearly to 0°.

When the temperature and pressure had been satisfactorily adjusted, the tap *C* was reversed, and the gas allowed to flow through the capillary tube leading to the previously exhausted decomposition bulb *M*. This bulb carried a silica boat slung from two stout platinum electrodes by means of silver leads; the boat was surrounded by a spiral of 30 per cent. iridium-platinum wire, which could be heated to redness by an electric current. The boat contained small pieces of pure aluminium.

In order to obviate the use of a ground joint necessitating a

* Both the taps *C* and *K*, through which hydrogen chloride passed, were lubricated with the paraffin grease described on p. 1639.

lubricant, the boat and its attachments were sealed up in the bulb before the latter was fixed *in situ*. When the two volumes of hydrogen chloride had been transferred, mercury was taken through the tap *C* and along the capillary as far as the bulb. During decomposition, the capillary leading to the pump was kept filled with mercury, previously introduced through the side-tube *Y*. This served to confine the hydrogen chloride to the bulb, and also to protect the lubricant of the tap *O* from the action of the gas. We might mention here that in our final experiments no gas but pure hydrogen was ever allowed to pass the tap *O* leading to the pump.

After decomposition, the resulting hydrogen was allowed to flow back through the tap *C* into the pipette, and the remainder taken through the pump into the collector *P*, which was sealed to the inverted end of the capillary fall-tube. From time to time the hydrogen in the collector was allowed to return by the capillary tube *R* to the pipette. As has already been indicated, the recovery of the original pressure was effected by running out mercury from the tap *S*, and so increasing the pipette volume. This volume increment was then accurately measured by weighing the mercury run out.

Decomposition of the Hydrogen Chloride.

The selection of a suitable metal for the decomposition of hydrogen chloride was a problem of some difficulty. Those metals forming chlorides reducible at a red heat by hydrogen were clearly unsuitable. For the process to take place readily, it was necessary that a clean metallic surface should always be exposed to the gas. To ensure this, the resulting chloride had to be either fusible or capable of being sublimed, or the metal had to be in the liquid state so that it could be agitated during the process.

Preliminary trials were made with the following metals: magnesium, tin, sodium amalgam, and, lastly, aluminium. With magnesium, the reaction did not start easily, and, once started, was quite uncontrollable. Molten tin reacted more gently, but with the dry gas the reaction did not proceed to completion. In the case of sodium amalgam, no decomposition whatever occurred unless the reaction vessel was appreciably moist. Even on raising the temperature to about 200°, the bright surface of the amalgam remained untarnished. In carrying out the reaction in presence of moisture, the hydrogen yield was too small. This probably is to be attributed to the fixation by the sodium hydroxide of a portion of the water, which did not then react with the amalgam.

Experiments with aluminium gave far more satisfactory results. Whilst there was no reaction in the cold, at dull redness and in

entire absence of moisture decomposition proceeded steadily and rapidly to completion. We therefore selected this metal for our final analyses.

The aluminium employed was a very pure specimen obtained from the British Aluminium Company. Analysis showed that it contained no carbon, a trace of iron, and only 0.1 per cent. of silicon. As is well known, aluminium electrodes, when subjected to the electric discharge in a vacuum tube, evolve hydrogen in appreciable quantities. The metal we used evolved a relatively small quantity of this gas, but the evolution was slow, even at bright redness in a vacuum. In order to reduce this content of hydrogen to negligible proportions, the silica boat and metal were kept at a high temperature in the evacuated bulb for several hours before a series of experiments was begun. Finally, the temperature was raised, and the aluminium just fused, which ensured the expulsion of the last traces of the gas. The silica boat was practically unattacked by the fused aluminium or by the subsequent treatment it underwent in the decomposition bulb, and its weight, even after a series of experiments, was hardly altered.*

During decomposition, the chloride volatilised as it was formed, and was deposited as a colourless, crystalline sublimate on the walls of the bulb, which were kept cold by a stream of water. The resulting hydrogen, when slowly bubbled through a silver nitrate solution, proved to contain no trace of hydrogen chloride. If, however, the aluminium chloride was first resublimed by heating the walls of the bulb, the hydrogen pumped off undoubtedly contained traces of the original gas. This showed that a certain quantity of hydrogen chloride had been retained by the sublimate; this occluded gas could not be pumped off, but was expelled during volatilisation. To eliminate this source of error, the aluminium chloride was sublimed in a vacuum after the main bulk of the hydrogen had been removed, and the small quantity of hydrogen chloride liberated was then decomposed by reheating the aluminium. This process was repeated until no more gas could be obtained. The final glowing served also to expel any gas which might have been taken up by the platinum-iridium wire on cooling in hydrogen at a high pressure.

In the earlier experiments, a wire of pure platinum was used for heating the boat, but we found that owing to the action of the aluminium vapour the wire fused after a short time and the circuit was interrupted. Renewal of the wire required the breaking and resealing of the end of the bulb, and caused much delay. By

* Original weight of boat.....	4.6715 grams	} Loss per experiment, 0.00003 gram
Weight after seven experiments	4.6712 "	
" " nine more experiments.	4.6710 "	

the employment of a wire containing a high percentage of iridium, drawn for us by Messrs. Johnson and Matthey, this difficulty was overcome. Frequent openings of the bulb entailed other disadvantageous consequences. The admission of moist air, even when no aluminium chloride was present, invariably led to irregular results, doubtless on account of the difficulty of drying the glass surfaces before the actual decomposition was begun. For this reason, sufficient aluminium for a series of determinations was introduced into the bulb at the start, and, with proper precautions to eliminate moisture, concordant values were usually obtainable after the first analysis.

From the foregoing description, it can be seen that in this apparatus the errors of measurement of the volume of the gas were reduced to a minimum. There was no appreciable uncertainty in the temperature of the manometer column, and the pressure was constant within the small limits defined by the accuracy with which the mercury surfaces could be set to the two points. The internal diameter of the glass tubing of which the reading portions of the manometer were constructed was about 15 mm. The capillary depression was consequently very small, and its influence on the pressure setting must have been quite negligible on account of the method of adjustment of the menisci. Further, it was repeatedly proved that the gas could be circulated through the apparatus and retransferred to the pipette with hardly any perceptible change in volume. Before the final determinations recorded in this paper, we spent more than two months in testing the apparatus. We frequently made the experiment of passing a measured volume of hydrogen prepared from hydrogen chloride into the decomposition bulb, heating the aluminium for a long period, and then measuring the gas again in the pipette. In absence of moisture, the two measurements never differed by more than one part in ten thousand, and in many cases a concordance of one part in twenty thousand was attained. In the actual analysis of hydrogen chloride, many unforeseen sources of error made their appearance, and these will now be briefly considered.

Impurities in the Hydrogen Chloride.

In discussing the purity of the gas with which the density determinations were made, we pointed out that a rigorous fractionation of the liquefied hydrogen chloride was necessary in order to remove traces of hydrogen sulphide from gas generated from sulphuric acid and a chloride. The results of the volumetric analysis indicated still more clearly the need of the same precaution, since an amount of this impurity, insufficient to affect the density,

had a marked influence on the volume ratio. That we finally succeeded in eliminating hydrogen sulphide is shown by the fact that nearly identical results were obtained by analysis of gas from silicon tetrachloride and water, and from phosphoric acid and ammonium chloride, sources which admitted of no possible contamination with this impurity.

Although the gas prepared from silicon tetrachloride and water had given excellent density results, a fresh preparation for the volume ratio apparatus was not so satisfactory. The difficulty of separating by fractionation some impurity the nature of which we were unable to determine soon led us to discontinue experiments with this particular sample of gas. From the lower-boiling fractions, we obtained one result which we have included in our final series, but the higher-boiling fractions gave values differing from each other by as much as one part in 2500, and were hence neglected. It was judged sounder to check our results by the analysis of gas from a fresh source rather than prepare another sample from silicon tetrachloride and water. Accordingly, we selected the interaction of phosphoric acid and ammonium chloride as likely to yield a pure product. The phosphoric acid (Kahlbaum, sp. gr. 1.7) contained no sulphates, no organic matter, no lower acids of phosphorus, and only a small trace of nitric acid, as shown by the brucine test. The ammonium chloride was a sample of very pure salt supplied by Merck, and contained no organic bases. It was recrystallised twice from boiling water, and the perfectly clear solution was then evaporated to dryness in the flask in which the reaction was afterwards carried out. The greatest care was taken to avoid the entrance of dust or other organic impurities. No corks were used, and evaporation was effected by the passage of a stream of pure dry air over the surface of the solution while the flask was heated on a water-bath. When the salt was perfectly dry, phosphoric acid was introduced, the neck of the flask sealed off, and the side-tube fused on to the rest of the apparatus. The reaction, which was carried out in a vacuum, proceeded steadily on gentle warming. The residue left in the flask after the reaction was always perfectly white. From its method of preparation, this specimen of hydrogen chloride must have been very pure. The liquefied gas, however, was subjected to the same series of distillations before storage as the less pure gas from other sources, and was fractionally distilled into the pipette immediately before analysis.

Among the list of impurities already discussed, we should include traces of sulphur dioxide and carbon dioxide, which might have been formed by the action of sulphuric acid on dust particles in

the reaction vessel. The existence of the former of these gases—which would have been easily separated by fractionation—is incompatible with that of hydrogen sulphide, small quantities of which were known to be present in the early stages of purification. Owing to its physical and chemical properties, traces of carbon dioxide would have escaped recognition or separation, but the presence of appreciable quantities would certainly have been detected, as the density and the volume ratio results would have been affected in opposite senses. Assuming that the carbon dioxide would have been completely reduced by the aluminium in the decomposition bulb, the volume ratio would have been low, whereas the density would have been high. The following table shows the effect of 0.1 per cent. by volume of various impurities on the density and volume ratio respectively:

	Density.	Volume of hydrogen from two volumes of hydrogen chloride.
Pure hydrogen chloride.....	1.6392	1.0079
0.1 per cent. H ₂ S	1.6391	1.0089
0.1 " air	1.6383	1.0085
0.1 " SiCl ₄	1.6423	1.0069
0.1 " CO ₂	1.6396	1.0069
0.1 " SO ₂	1.6405	1.0069
0.1 " HBr	1.6412	1.0079

It is easy to see that most impurities would have changed the results of the volumetric analysis and the densities in opposite directions and by different amounts. The fact that constant values for both sets of measurements were obtained with gas from different sources furnishes the best criterion of its purity and of the accuracy of our final numbers.

Adsorption of Hydrogen Chloride on the Glass Surfaces.

This phenomenon has already been discussed in Part I. A correction was made for the gas adsorbed on the walls of the density bulb and subsequently removed by the charcoal. In the same way the displacement by mercury of the hydrogen chloride from the pipette in the volume-ratio apparatus left on the walls a layer of adsorbed gas, which had to be taken into account, for had it not been removed it would certainly have escaped from the walls when the bulb was filled with hydrogen. In this case, however, it was unnecessary to measure and allow for this gas, since it could be got rid of without difficulty. In order to avoid any variation in the quantity of gas adsorbed, each volume of hydrogen chloride was transferred from the pipette to the decomposition bulb at approximately constant pressure. This was achieved by a suitable regulation of the tap *C* and of the position of the reservoir *D*, and

by carrying out the decomposition of the first volume of hydrogen chloride before the introduction of the second. As soon as the second volume of gas had been displaced, the tap *C* was shut and the reservoir *D* lowered. The adsorbed gas escaped from the walls into the vacuous pipette, and on taking the mercury up again was collected in the capillary. From here it was removed into the fractionating train by forcing the mercury through the other bore of the tap *C*. By repeating this operation twice, the adsorbed gas was reduced to a negligible quantity. In most experiments we adopted the further precaution of washing out the pipette with hydrogen from a previous determination.

Impurities in the Hydrogen.

The purity of the hydrogen obtained from the volume analysis was tested in various ways. The gas had no odour, and, as has already been mentioned, contained no trace of hydrogen chloride. The absence of hydrocarbons was proved by exploding with oxygen, when no carbon dioxide was found. Traces of silicon compounds, such as silicon tetrachloride, silicochloroform, or silicon hydride, might conceivably have been derived from the small quantity of silicon in the aluminium. Of these, silicon tetrachloride or silicochloroform would have been detected in the same manner as hydrogen chloride when the hydrogen was bubbled through silver nitrate solution. Silicon hydride, being very unstable, would hardly have escaped decomposition in the bulb. Further, on exploding the hydrogen with oxygen, any silicon compounds present would have left a residue of silica, and this was never observed.

In order to test for the presence of nitrogen, about 150 c.c. of the hydrogen were exploded with pure oxygen, until the volume was reduced to less than 1 c.c. This residue, after being dried over phosphoric oxide, was taken into a vacuum tube and examined spectroscopically. At low pressures no nitrogen could be detected, and there was only a very faint indication of its presence when the pressure was raised. This amount was negligibly small, and could not have influenced the results.

Numerical Results.

Since the volume, pressure, and temperature of the hydrogen chloride and the pressure and temperature of the resulting hydrogen were fixed and constant, the weight of the mercury run out of the volume-adjuster was a direct measure of the increase in volume, no corrections being required.

Volume of Hydrogen Chloride, 306.849×2 c.c. in all cases. *Volume of Hydrogen*, $306.849 + x$ c.c.

Source of gas.	Exp.	Weight of mercury run out (in grams).	Increment volume x (in c.c.).	Volume of hydrogen from two volumes of hydrogen chloride.
NaCl and H ₂ SO ₄ ...	1	33.25	2.446	1.00797
NaCl and H ₂ SO ₄ ...	2	33.16	2.439	1.00795
NH ₄ Cl and H ₂ SO ₄ ...	3	32.98	2.425	1.00790
NH ₄ Cl and H ₂ SO ₄ ...	4	32.97	2.425	1.00790
NH ₄ Cl and H ₂ SO ₄ ...	5	32.57	2.396	1.00781
SiCl ₄ and H ₂ O	6	32.50	2.390	1.00779
NH ₄ Cl and H ₃ PO ₄ ...	7	32.85	2.416	1.00787
NH ₄ Cl and H ₃ PO ₄ ...	8	33.30	2.449	1.00798
			Mean	1.00790
Maximum deviation, 1 in 5000.			Probable error, ∓ 0.000017 .	

We now have all the requisite data for calculating the atomic weight of chlorine.

If D_{HCl} represents the weight of a litre of hydrogen chloride at 0° and 760 mm., Lat. 45° , and D_{H} represents the weight of a litre of hydrogen under the same conditions, and if the ratio of the volumes of hydrogen and hydrogen chloride, which at 0° and 760 mm. contain equal number of molecules, is denoted by R , then the molecular weight of the gas in terms of $\text{O}=16$ is given by the expression:

$$\left\{ \frac{D_{\text{HCl}}}{D_{\text{H}}} \cdot \frac{2}{R} \right\}. \text{ Atomic weight of hydrogen.}$$

Assuming Morley's value for the weight of the litre of hydrogen under standard conditions, namely, 0.089873 gram, and also his value 1.00762 for the atomic weight of this element on the oxygen standard, the molecular weight of hydrogen chloride is obtained on substituting our experimental values in the above expression:

$$\frac{1.63915}{0.089873} \cdot \frac{2}{1.00790} \cdot 1.00762 = 36.467.$$

and the atomic weight of chlorine = 35.459.

This value is in close agreement with the values found by Dixon and Edgar, namely, 35.463, and by Edgar, 35.461, who also based their calculations on Morley's atomic weight of hydrogen, but differs by 1 part in 3500 from that found by Noyes and Weber, namely, 35.452, whatever value is assigned to hydrogen. It should be pointed out here that our result, unlike Dixon and Edgar's, is dependent not only on the atomic weight, but also on the density of hydrogen. We have selected Morley's value for this constant as being the most trustworthy, and our selection seems justified by

the results of the measurement of the compressibility of hydrogen chloride which we now proceed to describe.

PART III.—*The Compressibilities of Oxygen and Hydrogen Chloride*

It has been shown by D. Berthelot and Rayleigh that at sufficiently low pressures all gases should strictly follow Boyle's law, and that their relative densities should be exactly proportional to their molecular weights. The actual measurement of gaseous densities at low pressures is unnecessary, for the normal densities can be reduced to the corresponding values for perfect gases from a knowledge of the gaseous compressibilities. Thus, if D_1 represents the normal density of a gas, and A_{10}^1 the mean coefficient of compressibility between 1 and 0 atmospheres, then $D_1(1 - A_{10}^1)$ represents the density the gas would have under normal conditions if its behaviour on compression from very low pressure to 1 atmosphere were theoretically perfect. That is to say, the ratio of the molecular weights of different gases is exactly equal to the ratio of the densities:

$$D_1(1 - A_{10}^1) : D_2(1 - A_{20}^1) : D_3(1 - A_{30}^1), \text{ etc.}$$

The compressibility coefficient represents the deviation per atmosphere of a gas from Boyle's law between the pressure limits 0 and 1 atmosphere, and is defined by the expression:

$$A_{10}^1 = \frac{p_0 v_0 - p_1 v_1}{p_0 v_0 (p_1 - p_0)},$$

where v_1, v_0 represent the volumes occupied by the same mass of gas under pressures p_1, p_0 , at constant temperature. The densities $D_1(1 - A_{10}^1)$, $D_2(1 - A_{20}^1)$, etc., are called by D. Berthelot limiting densities.

The variation of gases from Avogadro's law may be conveniently expressed in terms of density per unit pressure. If the weight of a certain mass of gas is W grams, and if it occupies at 0° a volume V litres under a pressure of p atmospheres, its density per unit pressure is W/pv . The value taken by this expression when $p=1$ atmosphere represents the normal density, and the value when p is very small, the limiting density. At pressures intermediate between 0 and 1 atmosphere the same mass of gas will occupy the volumes v_1, v_2 , and v_3 , and exert the pressures p_1, p_2 , and p_3 , and the densities per unit pressure will be:

$$\frac{W}{p_1 v_1}, \quad \frac{W}{p_2 v_2}, \quad \text{and} \quad \frac{W}{p_3 v_3}.$$

For a perfect gas it is clear that these values will be equal, for pv is independent of the pressure, but for those gases which are more compressible than theory demands, pv increases as the pressure falls and the density per unit pressure diminishes. On the other hand, for gases like hydrogen and neon, the converse is true, and the limiting densities are greater than the normal densities.

The ratio of the limiting densities of two gases in this terminology is:

$$\frac{D_1}{D_2} = \frac{W_1}{p_0^1 v_0^1} \cdot \frac{p_0^2 v_0^2}{W_2},$$

where W_1 and W_2 represent any weights of two different gases in grams, and $p_0^1 v_0^1$, $p_0^2 v_0^2$ the values in litre atmospheres of the corresponding pv products of these weights at very low pressures. Consequently, if the molecular weights of the two gases are represented by M_1 and M_2 , and the molecular weight M_2 is known, the value of M_1 is given by the expression:

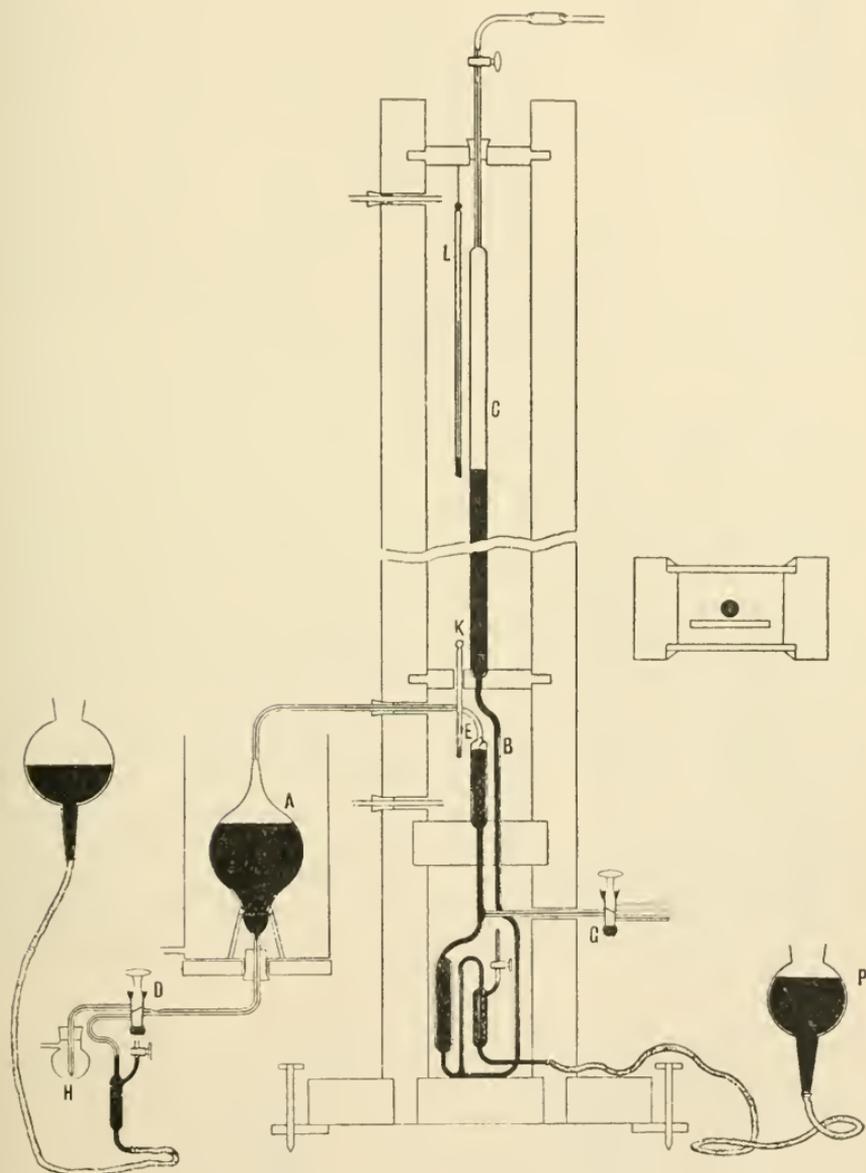
$$M_1 = M_2 \cdot \frac{W_1}{p_0^1 v_0^1} \cdot \frac{p_0^2 v_0^2}{W_2}.$$

It is, therefore, evident that the measurement of the exact molecular weights of gases by the method of limiting densities resolves itself into the accurate determination of the factor $p_0 v_0$. The whole problem, then, is to determine with the necessary precision the variation of pv between the pressure limits 0 and 1 atmosphere.

There are two ways in which pv can change with changing pressure. The variation per unit pressure may remain constant down to very low pressures, or the variation of pv may decrease. It is, however, very difficult to decide experimentally whether dpv/dp ever becomes zero, because as the pressure falls the measurement of p becomes less and less accurate. At very low pressures a gas may apparently obey Boyle's law; that is to say, if the volume be doubled, the pressure may appear to be exactly halved, but on account of the slight absolute change of p , the variation of pv may escape detection. For this reason, it is difficult to say from the researches of Rayleigh on the behaviour of gases at low pressures whether dpv/dp remains constant from one atmosphere down to very low pressures, or whether its value decreases as the pressure falls. All methods of determining the value of $p_0 v_0$ involve an extrapolation from regions where pv measurements are experimentally practicable. It is, therefore, essential to determine the lie of the pv isothermal in these regions as exactly as possible. In making the necessary extrapolation in order to calculate the exact molecular weights, most investigators have assumed either that pv is a linear function of p between the

limits 1 and 0 atmospheres, or that the slight curvature of the isothermal can be calculated from theoretical considerations (Guye, *J. Chim. phys.*, 1908, **6**, 769, and D. Berthelot, "Sur les Ther-

FIG. 4.



momètres à gaz"). The first assumption is very probably correct for the permanent gases, but for the more compressible gases, such as hydrogen chloride, the true form of the isothermal can only be

satisfactorily ascertained by the experimental determination of a large number of points. In their researches on the compressibilities of ammonia and sulphur dioxide, Jaquered and Scheuer made only three measurements of pv at pressures of 800, 400, and 200 mm. respectively, and extrapolated to zero pressure by means of a parabolic formula. The values they obtained in this way for the molecular weights of the two gases were distinctly too low, and it seems possible that the true form of the isothermal escaped recognition on account of the small number of points.

Another factor which has been neglected by all investigators in this connexion is the variation in the amount of gas adsorbed by glass surfaces with varying pressure. In the present investigation we have endeavoured to settle as accurately as possible the pv isothermals of oxygen and hydrogen chloride by determining a large number of points, and in the case of hydrogen chloride we have taken into account the adsorption effect.

A series of pressure and volume measurements were made between the pressure limits of 860 and 150 mm. Our results for oxygen confirm those of previous investigators, and show that the isothermal at 0° is a straight line within the limits of measurement. In the case of hydrogen chloride, the isothermal shows a distinct curvature, which becomes more marked as the pressure decreases.

The apparatus (Fig. 4) consisted essentially of a bulb *A*, connected with a dead-space *B* and manometer *C*. The effective volume of the bulb *A* could be varied by withdrawing mercury from the tap *D*. The bulb, which was made of thick glass, had a capacity of about 550 c.c., and was filled with mercury to a mark *E* on the capillary immediately above the dead-space. The pressure contraction of the bulb was measured by completely exhausting it, filling it with mercury cooled to 0° to a mark on the capillary stem, and then determining the change in volume with changing pressure by the movement of the meniscus along the graduated capillary. The results were expressed in a graph, from which the necessary volume correction for any given pressure could be read.

Experimental Numbers.

Pressure.	Volume to be subtracted from volume of gas.
760 mm.	0.000 c.c.
600 "	0.006 "
550 "	0.008 "
350 "	0.014 "
40 "	0.025 "

At the end of the compressibility measurements, we made experiments to see whether the weight of mercury in the bulk caused any

distortion involving alteration of volume. This was done by weighing out mercury and at the same time sucking in water through the upper capillary. The volumes corresponding with the successive quantities of mercury removed were compared with the volumes of water weighed in. Only a very small and negligible alteration in volume due to distortion was observed.

The dead-space and manometer were made from carefully selected lead glass barometer tubing, which had an internal diameter of about 17 mm. The use of lead glass tubing, on account of its freedom from bubbles and striæ, allowed the position of the meniscus to be determined with very great accuracy. In making the dead-space, special care was taken to avoid heating the glass immediately opposite the point. After many unsuccessful attempts, a dead-space possessing a volume of only 1.275 c.c. was obtained, and when it was placed in front of a glass scale and viewed through a low power microscope, no distortion of the scale lines in the vicinity of the point could be detected.

Dead-space and manometer were immersed in a bath with two plate glass sides, and a stream of water kept the temperature constant. Inside the bath and immediately in front of the manometer column was suspended a glass millimetre scale, to which the distance between the two mercury menisci was referred. The scale, which was 1200 mm. long, was made by the Société Gènevoise. The lines were of the order of 0.002 mm. in thickness, and required careful illumination to render them visible. For measuring fractions of a millimetre, we used a telescope fitted with a Hilger micrometer eye-piece, which enabled an accuracy of 0.01 mm. to be obtained. The length of scale over which readings were taken (960 mm.) was compared with an "invar" standard, and found to be 0.044 mm. too long at 16°. The scale was further calibrated in 30 mm. lengths by means of a reading microscope and standard screw reading to 0.001 mm., and a table of deviations drawn up. The maximum correction for irregularity of the scale was 0.03 mm.

EXPERIMENTAL.

The oxygen was prepared by heating pure potassium permanganate, and was purified and dried by passage over soda-lime and phosphoric oxide. It was finally liquefied and distilled into the bulb. The hydrogen chloride was prepared and purified in the way already described. Before the final filling, the bulb was repeatedly exhausted and washed out with the gas to be experimented with. It was then filled with mercury rather beyond the mark *E* on the capillary above the dead-space, and the whole cooled to 0°. The gas entered the dead-space through the side-tube *G*,

and when the pressure had risen to atmospheric, the final adjustment of the meniscus to the mark on the capillary was made by means of the tap *D*. By making this final adjustment at atmospheric pressure we obviated the necessity of applying a correction to the original volume of the gas for the contraction of the bulb on exhaustion. The next step was to allow mercury to run out of the tap *D* into a weighed bottle *H* until the effective volume of the bulb was of the required magnitude. The quantity of gas in the bulb and dead-space could then be adjusted, so that when the mercury meniscus was set to the glass point the pressure was of the order desired. By working in this manner, the initial volume of the gas was given directly by the volume of the mercury at 0° withdrawn from the bulb, plus the volume of the dead-space.

Before reading the pressure of the imprisoned gas, we waited for some time after the temperature of the water in the manometer bath had ceased to vary. After a constant temperature gradient had been attained, there was usually a small difference of the order of 0.1° between the water surrounding the dead-space and the water at the top of the bath. The temperature of the water was ascertained by means of two thermometers, *K* and *L*, inside the bath, one fixed close to the dead-space point, and the other adjustable to the level of the upper mercury meniscus. At low pressures the thermometers showed an almost perfect agreement, since they were closer together. The temperature of the bath remained constant for long periods, and since the mean temperature was certainly known to within 0.05° , the maximum error on the length of the mercury column due to uncertainty of temperature was less than 0.01 mm.

The reduction of the temperature of the bulb and its contents to 0° was necessarily slow, but by observing whether the mercury meniscus in the dead-space remained set, it was easy to see when equilibrium had been established. To avoid uncertain correction, that part of the capillary tube which was outside the bath, and connected the bulb and dead-space, was also immersed in melting ice contained in a metal gutter.

Before making a pressure reading, the mercury meniscus in the dead-space was always brought exactly in contact with the point by means of a screw clamp compressing the rubber tubing connecting the reservoir *P* with the dead-space and manometer column. The distance of a line on the scale from the set meniscus was verified immediately before and after each reading, as it was found that the position of the scale was subject to minute variations. Except that we always adjusted our mercury meniscus exactly to the glass point, our method of reading was the same in all particulars as the method described by Travers, Senter, and Jaquero

in their research on the coefficients of expansion of helium and hydrogen. On account of the relatively large diameter of the mercury meniscus, the point and its mirror image were visible through the telescope, so that an exceedingly accurate setting was possible; further, the correction for capillarity was reduced to negligibly small dimensions.

The initial pressure having been determined, successive quantities of mercury were withdrawn from the bulb and weighed, and the pressures corresponding to the new volumes read. As can be seen from the diagram, mercury would cease to flow from the tap *D* after the pressure in the manometer had fallen to about 500 mm. At this stage, mercury was withdrawn by attaching the side-tube of the small flask *H* to a filter pump. When nearly all the mercury had been removed from the bulb, the process was reversed, and a series of readings taken with rising pressure.

The results in the following table are stated with all corrections made. The latter comprise:

For volume.

1. Reduction of the volume occupied by the gas in the dead-space to 0°.
2. Contraction correction of the bulb.
3. Reduction of the apparent weight of mercury to the vacuum standard.

For pressure.

1. Correction for the total error in the scale at the temperature of reading.
2. Correction for irregularity of ruling in the scale.
3. Reduction of the corrected manometric height to 0°.

In order to show how the corrections were applied, we append a full calculation of the results of one experiment taken at random from our note-book.

Oxygen.

Series I.

<i>p</i> (in mm.).	<i>v</i> (in c. c.).	<i>pv</i> .	Smoothed <i>pv</i> .
763·52	182·864	139620	139629
711·07	196·373	139635	139638
612·56	227·980	139651	139656
564·46	247·440	139670	139665
499·93	279·400	139680	139677
447·18	312·393	139696	139687
384·52	363·300	139696	139696
348·83	400·456	139691	139705
313·57	445·585	139722	139712
284·77	490·603	139709	139717

Series II.

p (in mm.),	v (in c.c.),	pv .	Smoothed pv .
875.99	158.611	138942	138940
849.32	163.605	138953	138945
826.60	168.106	138956	138949
778.09	178.587	138957	138956
738.03	188.304	138974	138962
690.64	201.212	138965	138970
609.03	228.204	138983	138983
560.45	248.010	138997	138992
515.32	269.724	138994	139000
409.56	339.420	139013	139018
372.85	372.842	139014	139024
337.27	412.177	139015	139031
309.58	449.115	139037	139035
280.52	495.651	139040	139040
256.73	541.616	139049	139044

Series III.

866.99	64.874	56245	56249
785.76	71.597	56258	56255
607.97	92.570	56280	56267
547.05	102.863	56271	56272
488.03	115.302	56271	56276
426.36	131.996	56278	56280
365.61	153.959	56289	56285
322.83	174.367	56291	56288
282.72	199.102	56290	56290
252.53	222.920	56294	56293
226.33	248.730	56295	56294
204.30	275.575	56300	56296
188.54	298.563	56291	56298
185.87	302.916	56303	56298
171.66	327.945	56295	56299
169.39	332.375	56301	56299
157.48	357.468	56294	56300

Calculation of pv at 0° from experimental results (last in Series III).

Volume of Gas.

Volume of gas in bulb at previous reading, all corrections made		328.807 c.c.
Weight of mercury run out.....	373.25 grams	
Correction for air displacement of mercury ...	+0.03 ,,	
Increase in effective volume of bulb	373.28	= 27.456 ,,
Volume of dead-space	13.5955	
Temperature of gas in dead-space	1.275 c.c.	
Volume of gas in dead-space at 0°	11.00°	
Contraction of volume of bulb under diminished internal pressure, namely, 158 mm.	$\frac{1.275 \times 273}{284}$	= 1.226 ,,
Total volume occupied by gas at 0°		-0.021 ,,
		357.468 c.c.

Pressure of Gas.

Lower Meniscus.—Mean of two series of readings taken before and after reading upper meniscus:

	Micrometer readings.	Millimetre.	Scale readings.
Distance from mercury meniscus set to point in dead-space to scale-line 5 above it	92, 89, 89, 91,	0.70	5.60 - 0.70
	91, 89, 89		= 4.30
	Mean = 90 (128 micrometer divisions = 1 mm.)		

Upper Meniscus:

Distance of upper meniscus below scale- line 163	111, 113, 112 Mean = 112	0.88	163.00 - 0.88 = 162.12
Uncorrected manometric height	162.12 - 4.30	=	157.82 mm.
Correction for total error in scale	0.044×158 960	=	+ 0.007
Contraction of scale from 16° to 11°	$0.000009 \times 5 \times 158$	=	- 0.007
Correction for irregularity of scale ruling		=	- 0.021
Correction of observed manometric height from 11.05° to 0°		=	- 0.320
Corrected manometric height		=	<u>157.48 mm.</u>

Therefore, $pv = 157.48 \times 357.468 = 56294$.

The experimentally found values of pv for each series were plotted on squared paper on an open scale against the corresponding pressures, and it was found that the points were evenly distributed about a straight line. Various lines were ruled, until one was obtained which was judged to approximate most closely to the positions of the largest number of points. The deviations of the points from this line were read off and summed. This process was repeated, if necessary, with a fresh line until the algebraic sum of the deviations approached zero. From the final line the smoothed values for pv given in column 4 were obtained. From the table it can be seen that, although a few of the points diverge appreciably, yet the majority deviate only slightly from the smoothed values, and the position of the final line, on account of the number of points, is fixed with a high degree of accuracy.

From the three series, the corresponding values of p_0v_0 and p_1v_1 are readily obtained:

Series.	p_0v_0 .	p_1v_1 .
1	139769	139628
2	139087	138959
3	56311	56256

The limiting densities are given by the expression:

$$D_{\text{lim.}} = \frac{W}{p_0v_0},$$

where W equals the weight of gas in grams, and p_0v_0 is expressed in litre-atmospheres.

But $W = \frac{D_{\text{norm.}} \cdot p_1v_1}{p_1}$, where $D_{\text{norm.}}$ is the weight of a litre under standard conditions, p_1v_1 is in litre-atmospheres, and $p_1 = 1$. Substituting $D_{\text{lim.}} = \frac{D_{\text{norm.}} \cdot p_1v_1}{p_0v_0}$, which is independent of the units in which pv is expressed, the limiting density of oxygen, assuming for the weight of a normal litre, lat. 45° , the value 1.42900 grams, is:

Series 1	1.42756
„ 2	1.42768
„ 3	1.42760
Mean, taking into account the number of observations in each series.....	1.42762

6 The compressibility coefficient A_0^1 from each series is:

Series 1	-0.001009
„ 2	-0.000920
„ 3	-0.000977
Mean	-0.000964

The pv measurements in the case of hydrogen chloride were obtained in a precisely similar way to those just described, but in calculating out the results, a further correction was applied for adsorption of the gas on the walls of the bulb. The maximum volume of gas adsorbed at 0° and 760 mm. was determined in the bulb itself, which for this purpose replaced one of the glass cylinders shown in Fig. 5. Afterwards the variation of the quantity of gas adsorbed with varying initial pressure was measured in the apparatus about to be described, and these experiments, in conjunction with the experiment in the bulb, enabled the requisite corrections for all pressures to be applied to the compressibility measurements.

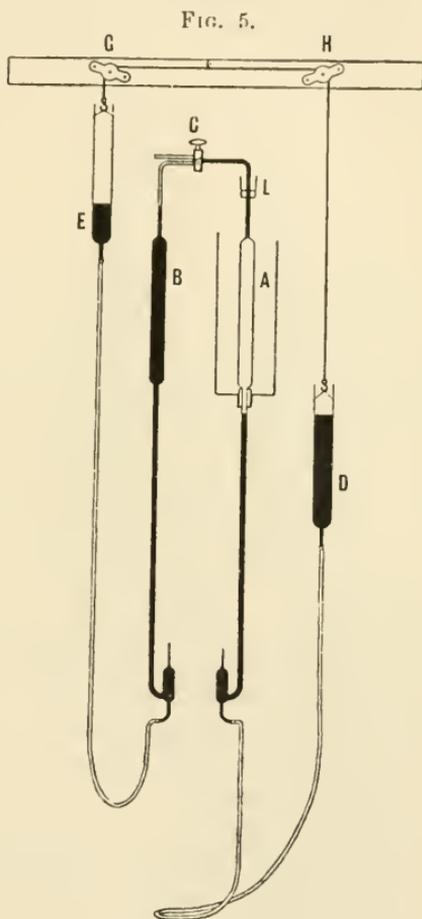
The principle of the method was to expose the surface of a dry glass cylinder to hydrogen chloride at a definite temperature and pressure, and then to displace the gas at constant pressure by mercury. The adsorbed gas remained on the glass below the surface of the mercury, and was subsequently removed by lowering the mercury and producing a Torricellian vacuum in the cylinder. Finally, the volume of the adsorbed gas was measured in a capillary tube.

The apparatus (Fig. 5) consisted of two cylinders, A and B , of about 300 sq. cm. internal surface, connected with each other through a two-way stopcock C . The cylinders could be filled with mercury from the reservoirs D and E , which were attached to a

cord running over the pulleys *G* and *H*. This system of adjustment enabled one to transfer the gas from one cylinder to the other at constant pressure. The cylinder *B* was not used in the measurements, and merely served as a reservoir for the collection of the displaced gas. The measuring cylinder *A* was surrounded with ice and water contained in a tin-bath, and the capillary tube *K*, which was carefully calibrated, was used for the measurement of the volume of the adsorbed gas.

Before the hydrogen chloride entered the apparatus, the greatest care was taken to ensure the complete absence of moisture. The gas was left in contact with the glass for twenty-four hours, and then displaced into the cylinder *B* at constant pressure. The tap *C* was then turned off, and a short length of the mercury thread in the calibrated capillary was frozen by means of solid carbon dioxide contained in the paper vessel *L*. This was necessary, because the gas dissolved in the grease of the tap, and was afterwards slowly evolved in a vacuum. The mercury was next lowered so as to produce a vacuum, into which the adsorbed gas escaped. On allowing mercury to refill the cylinder, this gas was collected and measured in the capillary, and was afterwards removed through the tap *C*.

The mercury thread was then frozen again, and by repeating the operations described, a further quantity of gas was collected and measured. This process was continued, allowing definite intervals of time for the adsorbed gas to accumulate, until the volume obtained became negligibly small. The measured volumes of gas were afterwards plotted against the times during which the surface remained exposed to a vacuum. By making measurements at different pressures, we obtained a series of curves from which the total volumes of gas adsorbed at various pressures



could be read. The logarithms of these volumes were finally plotted against the corresponding pressures, and the corrections to be applied to the volumes in the compressibility measurements were read from the curve so obtained.

Variation of Adsorption with Pressure.

Experiments in cylinder *A*; surface 300 sq. cm. $T=0^{\circ}$.

Pressure.	Volume of adsorbed gas at 0° and 760 mm.
0	0.0000
218 mm.	0.0034 c.c.
317 "	0.0045 "
547 "	0.0070 "
730 "	0.0104 "

The experiments in the bulb yielded for the same initial pressure a larger volume of gas per unit area. This was almost certainly due to a difference in the state of the surface of the glass, since the other experimental conditions were the same. The total quantity of gas adsorbed at a pressure of 782 mm. of mercury and at 0° was 0.047 c.c., and the surface was 320 sq. cm. In correcting our results, we have adopted the value obtained in the bulb itself, and for lower pressures we have multiplied the values from the cylinder experiments by a factor to correct them to this standard.

It should be stated here that experiments on the amount of adsorption of hydrogen and air were also made in this apparatus. With hydrogen the amount of gas adsorbed was barely detectable. Air was adsorbed to a greater extent, but the value obtained was very much smaller than that in the experiments with hydrogen chloride. These results are of interest, since they show that the gas was really adsorbed and not imprisoned in minute cavities in the glass surface.

Before correcting the results, one other factor had to be taken into account. Since the quantity of gas adsorbed is directly proportional to the surface, it was necessary to know how the surface of the bulb exposed to the gas varied as the mercury was withdrawn. For this purpose, we assumed that the bulb was spherical, and we calculated the surface for the corresponding volumes. The nature of the correction will be clear from the following figures, taken from the correction table in our note-book:

Pressure of gas.	Surface of glass exposed.	Volume of adsorbed gas at 0° and at observed pressure: to be added to measured volume of gas.
829 mm.	68 sq. cm.	0.0098 c.c.
314 "	122 "	0.0172 "
158 "	193 "	0.0341 "

As the glass surface increased and the pressure fell, the absolute amount of gas adsorbed also increased, since the surface effect more than counter-balanced the effect of diminishing pressure. The actual alteration of the form of the curve on applying this correction was very small.

The following table of results for hydrogen chloride is given with all corrections made:

Hydrogen Chloride.

p (in mm.).	v (in c.c.).	pv .	Smoothed pv .
829.50	66.012	54757	54757
761.09	72.023	54816	54802
734.65	74.626	54824	54820
720.78	76.072	54831	54829
604.71	90.815	54917	54903
558.67	98.334	54936	54932
515.35	106.642	54958	54958
468.21	117.432	54983	54986
424.66	129.525	55004	55010
384.13	143.259	55030	55034
347.70	158.343	55056	55054
314.29	175.233	55074	55072
289.39	190.331	55080	55084
264.53	208.286	55098	55097
243.40	226.401	55106	55107
223.95	246.117	55118	55116
207.68	265.447	55128	55125
193.41	285.016	55125	55132
180.24	305.898	55135	55138
157.57	349.978	55146	55148

On plotting pv against the corresponding pressures on the same scale as the oxygen, we found that a line drawn through the points had a slight but distinct curvature, which was more marked in the low pressure region. That is to say, the variation of pv per unit pressure decreases as the pressure falls, and the rate of decrease is greater at lower pressures. It seems probable that a compressibility curve of this type may be characteristic of all gases which at 0° lie below their critical points, and, if this is so, D. Berthelot's principle, when properly applied, should give as accurate results for the liquefiable as it does for the permanent gases (Guye, *J. Chim. phys.*, 1908, **6**, 792).

In drawing the most probable line through the points, exactly the same procedure was followed as in the case of oxygen. Two points in the high pressure region were obviously inaccurate, and less weight has been assigned to them than to the other points. On account of the slight curvature, extrapolation to zero pressure seemed at first sight an uncertain process. Afterwards, when the general lie of the curve had been fixed by means of a spline, graphic extrapolation over the comparatively short length of 157 mm. gave values for p_0v_0 differing only slightly from each other. After many

trials, we decided that the fairest extrapolation was obtained with the curve cutting the pv axis at 55213. The value of p_1v_1 , also taken from this curve, proved to be 54803, so that the value given by the results for

$$\frac{p_0v_0}{p_1v_1} \text{ is } \frac{55213}{54803} = 1.00748,$$

and the limiting density of hydrogen chloride is

$$\frac{D_{\text{norm.}} \cdot p_1v_1}{p_0v_0} = \frac{1.63915}{1.00748} = 1.62698 \text{ grams per litre at } 0^\circ \text{ and } 760 \text{ mm.}$$

The molecular weight of hydrogen chloride in terms of oxygen is, therefore,

$$\frac{D_{\text{lim. hydrogen chloride}}}{D_{\text{lim. oxygen}}} \cdot 32 = \frac{1.62698 \times 32}{1.42762} = 36.469,$$

and the atomic weight of chlorine, $36.469 - 1.0076 = 35.461$.

If the validity of the assumption underlying the principle of limiting densities be admitted, this result affords valuable confirmatory evidence of the correctness of the atomic weight of chlorine obtained by volumetric analysis. The two values, 35.459 and 35.461, only differ by 1 part in 18,000. They both depend, however, on the density of hydrogen chloride, and any uncertainty in it would affect them equally. The former value, as is evident from the method of calculation, is further influenced by any error which would change the ratio atomic weight of hydrogen : density of hydrogen, but the latter number is practically independent of the O : H ratio, for the molecular weight of hydrogen chloride yielded by the compressibility results is expressed directly in terms of the oxygen standard. The close agreement is mainly brought about by the concordance of the results of the volumetric analysis and those of the pv measurements. Thus, if +0.00054 be taken as the coefficient of compressibility of hydrogen per atmosphere at 0° (the mean of the results of Rayleigh, Jaquerod, and Scheuer and Chappuis), the ratio of the volumes of hydrogen and hydrogen chloride containing equal numbers of molecules is:

$$\frac{1 + 0.00054}{1 - 0.00748} = 1.0081,$$

whilst volumetric analysis gave 1.0079.

The final value for the atomic weight of chlorine yielded by these investigations is, therefore,

$$35.460. \quad O = 16.$$

An arithmetic mean of all recent determinations (O=16; H=1.00762) gives the same result.

Dixon and Edgar	35.463
Edgar	35.461
Noyes and Weber	35.452
Richards and colleagues	35.457
Guye and Fluss	35.466
Guye and Ter-Gazarian.....	35.461
Gray and Burt	35.460
	<hr/>
Mean	35.460

Consequently, it may be stated with a considerable degree of certainty that the higher numbers which result from the use of Noyes' value for the atomic weight of hydrogen, namely, 1.00787, are distinctly too great, and that the value advocated by Brauner is a close approximation to the true atomic weight of chlorine.*

In conclusion, we desire to express our appreciation of the kindly interest Sir William Ramsay has taken in the research, and to thank him for his advice and criticism. Also we wish to thank Mr. H. S. Patterson and Mr. H. Page, who analysed some of the samples of aluminium, and Mr. W. N. Morley and Mr. A. C. Dunningham, who helped us in some of the compressibility measurements.

Part of the expense of the work was defrayed by a grant from the Royal Society, and we here record our indebtedness to the Government Grant Committee, without whose assistance this investigation could not have been made.

UNIVERSITY COLLEGE,
LONDON.

* During the correction of the proofs of this paper, a research by Scheuer on the density of hydrogen chloride has appeared (*Compt. rend.*, 1909, 149, 599). According to this he obtains for the weight of a normal litre of the gas the value 1.6394 grams. This only differs from our present figure, namely, 1.6392 grams, by 1 part in 8000. Possibly this small discrepancy may be due to the different method employed by us to correct for the gas adsorbed by the walls of the bulb.

We have already referred to the error affecting the results which we published in a preliminary note (*Proc.*, 1908, 24, 215).

CLXXXV.—*The Spontaneous Crystallisation of Solutions of Sodium Carbonate and Sodium Thiosulphate.*

By BERNARD MOUAT JONES.

DURING the investigation of the spontaneous crystallisation of solutions of sodium sulphate (Hartley, Jones, and Hutchinson, Trans., 1908, **93**, 825), it was found that if crystal nuclei were excluded, and the solutions of varying strengths cooled down slowly with constant shaking, the unstable hydrate, $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$, nearly always appeared. The production of this solid phase was very regular, and the conditions determining its appearance were exactly defined by the supersolubility curve that was traced for it. The work recorded below was undertaken in order to determine whether, in the case of salts which form several hydrates, the spontaneous production of the unstable form, when supersaturated solutions are slowly cooled and shaken, is a general phenomenon. The salts chosen for the investigation were sodium carbonate and sodium thiosulphate, both of which crystallise from aqueous solutions with amounts of water of crystallisation which vary according to the conditions.

I.—*Experiments on Solutions of Sodium Carbonate.*

Five solid phases may crystallise from solutions of sodium carbonate, namely, ice, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$ (orthorhombic), $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$ (rhombohedral), and $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$. The supersolubility curves (that is, the curves giving the temperature of spontaneous crystallisation of supersaturated solutions of varying strengths) have been traced for ice, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, and $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$. The crystallisation of $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$ (orthorhombic) was irregular and of rare occurrence, giving but a slight indication of a supersolubility curve in the case of this solid phase. The crystallisation of the rare rhombohedral $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$ was not observed at all.

The method of experiment was precisely similar to that used in previous investigations on sodium sulphate (Hartley, Jones, and Hutchinson, *loc. cit.*) and on some alkaline nitrates (Jones, Trans., 1908, **93**, 1739). Weighed amounts of pure anhydrous sodium carbonate and distilled water were sealed up in glass tubes containing angular fragments of Jena glass to promote friction. The tubes were then warmed in a bath until all traces of crystalline nuclei had disappeared. Care was taken not to warm the tubes to too high a temperature, in order to avoid the production of the

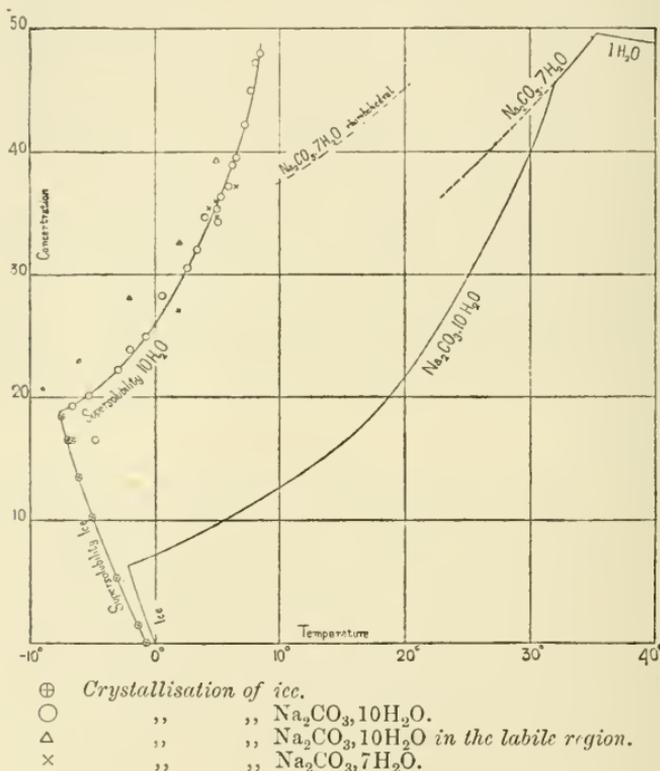
monohydrate which might act as a nucleus for the growth of one of the other hydrates. When it was certain that no solid salt remained in the tube, it was cooled down with constant shaking by hand in a well-stirred water- (or alcohol-) bath, the temperature of which was falling at the rate of about one degree in twenty minutes. The temperature at which crystallisation occurred was noted on a thermometer graduated in tenths of a degree, and standardised against a thermometer with a National Physical Laboratory certificate. Several determinations were made with each tube. After one preliminary determination with the temperature of the bath falling rather more rapidly, the remaining determinations rarely differed by more than one or two tenths of a degree. The highest temperatures at which crystallisation was observed for solutions of varying strengths are given in the tables below, and are plotted as supersolubility curves in the figures. In all cases the determinations were made as soon as possible after the sealing of the tube, in order to minimise the effects of the chemical action of the alkaline liquid on the glass. From the concordance of the results, it was evident that the amount of action was very small in tubes which had only recently been made up. In tubes which had been prepared some weeks, particles of silica could be seen in the liquid, and such tubes were not used in plotting the supersolubility curves.

Crystallisation of Ice.—This was an extremely definite phenomenon. The temperature of spontaneous formation of ice could generally be foretold to 0.1° . Very violent shaking did not seem to cause crystallisation at temperatures appreciably higher than those recorded with moderate shaking. Distilled water, cooled under exactly the same conditions as the sodium carbonate solutions, gave ice crystals at -0.7° . This temperature is rather higher than that previously found by the author, -1.2° (*loc. cit.*). The rate of cooling, however, in the present instance, was rather slower. The temperature observed by Miers was -0.4° , and by Hartley, Jones, and Hutchinson, -0.5° . The small difference between these values and the value -0.7° recorded in the present paper is probably due to the solvent action of the water on the glass fragments enclosed within the tube. These fragments become broken up by the continual shaking, and the very small particles of glass produced in this way are doubtless acted on by the water fairly rapidly, and lower slightly the temperature of the spontaneous production of ice. The value -0.5° was obtained by using garnets in place of glass fragments; Miers used "glass, garnet, galena, or lead." The use of glass as an agent to produce friction, then, probably introduces a slight constant error of not more than one

or two tenths of a degree into all the determinations. At the same time, its use is not attended with the disadvantages arising from crystallised substances, such as garnets or galena, which may have some inoculating effect, the extent of which it might not be possible to gauge, and which might vary for different solutions.

The highest observed temperatures of crystallisation of ice from dilute solutions of sodium carbonate are given in table I. They

FIG. 1.



are plotted as the ice-supersolubility curve in Fig. 1. It is seen that this curve runs nearly parallel to the ice-solubility curve at an average distance from it of about one and a-half degrees.

TABLE I.

(The tube contained from 1.8 to 4.4 grams of solution.)

Parts of Na ₂ CO ₃ in 100 parts H ₂ O...	0.0	1.50	5.31	10.26	13.53	16.50	16.57	18.46
Temp. of crystal- lisation of ice ...	-0.7°	-1.3°	-3.1°	-5.0°	-6.1°	-6.6°	-7.0°	-7.5

Two anomalous cases were observed, for which no explanation at present seems forthcoming. The tube of concentration 10·26 gave crystals of ice on slow cooling at $-5\cdot15^\circ$ and $-5\cdot05^\circ$. In the third experiment, crystals of $\text{Na}_2\text{CO}_3\cdot 10\text{H}_2\text{O}$ were produced at $-5\cdot0^\circ$. On dissolving these, and cooling down again, ice appeared as before at $-5\cdot05^\circ$. Attempts to produce salt again from this tube were not successful.

The tube of concentration 16·57 showed an even more curious behaviour. The supersolubility curve indicated that ice should be formed at about -7° . A preliminary rather rapid experiment gave crystals of $\text{Na}_2\text{CO}_3\cdot 10\text{H}_2\text{O}$ at $-7\cdot5^\circ$. A second slow experiment produced ice at $-7\cdot0^\circ$; but on removing the tube from the bath the ice melted, and salt suddenly appeared. Subsequent experiments with this tube gave salt always between $-4\cdot8^\circ$ and $-6\cdot0^\circ$. Ice was never again produced in this tube. Repetition of the experiments on the same tube two months later produced salt at about -7° , but in this case there were obvious signs that considerable chemical action had taken place in the interval. Another tube of nearly the same concentration, 16·50, was prepared. This behaved normally, always giving ice at about $-6\cdot6^\circ$.

Crystallisation of $\text{Na}_2\text{CO}_3\cdot 10\text{H}_2\text{O}$.—

TABLE II.

(The tube contained from 1·5 to 5·5 grams of solution.)

Parts of Na_2CO_3 in 100 parts H_2O .	Temperature of crystallisation of $\text{Na}_2\text{CO}_3\cdot 10\text{H}_2\text{O}$.	Parts of Na_2CO_3 in 100 parts H_2O .	Temperature of crystallisation of $\text{Na}_2\text{CO}_3\cdot 10\text{H}_2\text{O}$.
19·27	$-6\cdot6^\circ$	39·28	$+4\ 9^\circ$
23·01	6·0	35·38	5·0
20·24	5·3	34·23	5·1
22·26	3·0	36·38	5·3
23·87	2·0	37·20	5·9
28·09	2·0	38·95	6·2
25·09	0·7	39·58	6·5
28·34	$+0\cdot6$	42·42	7·2
32·57	2·0	44·92	7·7
30·56	2·6	47·30	8·0
32·03	3·4	47·98	8·4
34·71	4·0		

Table II shows the highest temperatures at which supersaturated solutions of sodium carbonate, on slow cooling and constant shaking, would deposit crystals of the decahydrate. In cooling such solutions, it was nearly always the decahydrate which appeared; the spontaneous formation of the heptahydrate was only rarely observed—in all, eight times in five tubes, out of a total of more than 100 crystallisations in which salt was produced. The regularity of the crystallisation of the decahydrate is indicated by the super-

solubility curve traced in Fig. 1, which determines the lower temperature limit of the metastable region for this solid phase. In no case did crystallisation of the decahydrate take place appreciably within the metastable region as defined by this curve—except in the two anomalous cases mentioned above. In a few cases, however, marked Δ on the diagram, it was necessary to cool the tubes a few degrees into the labile region before crystallisation would take place. The tubes for which this was necessary showed always a slightly anomalous behaviour. The tendency to crystallise seemed rather sluggish, and a longer time was necessary before crystallisation could be induced to take place. It is possible that in these tubes the glass fragments had been attacked to a greater extent by the alkaline solution than in the case of the normal tubes. In every abnormal case, when another tube was prepared of nearly the same concentration, the new tube behaved normally, the solution crystallising at the temperature required by the supersolubility curve. When crystallisation of the decahydrate occurred, it appeared to start from a few, generally one or two, points, which might be on the inner surface of the glass, or, less usually, in the interior of the solution itself. The crystallisation, having once started, proceeded with great velocity, the whole solution at once becoming solid.

The supersolubility curve for $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ is seen from the figure to lie roughly parallel to the solubility curve at an average distance from it of 25 degrees. It cuts the supersolubility curve for ice at a temperature of -7.6° , corresponding with a concentration of 18.7; this is the "hypertectic" point for ice and decahydrate.

Crystallisation of $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$.—As mentioned above, the appearance of this solid hydrate was of rare occurrence, and a tube which would give it once would not necessarily give it again. The highest observed temperatures of crystallisation of this phase are given in table III:

TABLE III.

(The tube contained from 2.9 to 4.1 grams of solution.)

Parts of Na_2CO_3 in 100 parts H_2O	27.11	34.71	35.38	36.00	37.20
Temp. of crystallisation of $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$.	1.9°	5.0°	4.3°	4.9°	6.5°

The first tube seems to have been abnormal. Crystallisation of the heptahydrate was observed once only at a much higher temperature than was anticipated, and the observation could not be repeated. Nor could the decahydrate be induced to appear even at temperatures well below 0° . Omitting this tube, it appears that there is a tendency to produce the heptahydrate only between

narrow limits of concentration—34·71 and 37·20. Even between these limits, however, the tendency to form the decahydrate was just as marked, the ratio of the number of crystallisations of heptahydrate to that of decahydrate being 8 : 7.

The crystallisation temperatures of the heptahydrate, shown on the figure thus: X, give a slight indication of the existence of a supersolubility curve for this hydrate, running nearly parallel to the solubility curve, but the crystallisation was not sufficiently regular or definite to make this certain. The opposing tendency among the solute molecules to produce the decahydrate appears to make the determination of the metastable limit for the heptahydrate a matter of some uncertainty.

The formation of the heptahydrate was characterised by the sudden production of a great number of small crystals, giving the solution a milky appearance. The production of this "labile shower" in the case of the heptahydrate was in marked contrast with the sudden solidification of the solution on the formation of the decahydrate.

Crystallisation of $\text{Na}_2\text{CO}_3, \text{H}_2\text{O}$.—This hydrate is less soluble in hot than in cold water; hence it is necessary to heat a saturated solution freed from crystal nuclei in order that crystallisation may take place. Owing to the negative temperature-coefficient, and to the fact that the solubility curve at higher temperatures becomes almost parallel to the temperature axis, the rate of adjustment of equilibrium in such a solution is extremely slow. The observation of the spontaneous formation of crystals was then in this case a more tedious and difficult matter. It was found necessary to use platinum tetrahedra to promote friction instead of glass fragments, since the latter on breaking up gave rise to minute particles indistinguishable from the crystals of the monohydrate. These latter, when first formed, were without definite outline, sharp edges, or bright facets, but were irregular, rounded, glassy particles, showing no distinctive characters under a pocket-lens. This fact rendered their immediate detection a matter of some difficulty. The lowest temperatures at which spontaneous crystallisation was observed in tubes of varying strengths are given in table IV. These temperatures are probably not accurate to less than one degree.

TABLE IV.

(The tube contained from 2·3 to 4 grams of solution.)

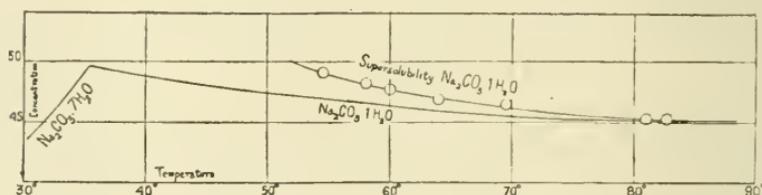
Parts of Na_2CO_3 in 100							
parts H_2O	49·06	48·23	47·72	46·90	46·52	45·34	45·30
Temp. of crystallisation of							
$\text{Na}_2\text{CO}_3, \text{H}_2\text{O}$	54·5°	58·0°	60·0°	64·0°	69·5°	81·0°	82·7°

The results are plotted in Fig. 2, and give rise to a supersolubility curve which at higher temperatures is almost coincident with the solubility curve.

II.—Experiments on Solutions of Sodium Thiosulphate.

Sodium thiosulphate has long been known as a salt which readily gives rise to strongly supercooled solutions or fusions. It is, further, a salt which forms a number of different solid hydrates, and so was considered suitable for the present investigation. The crystallisation of supercooled fusions of this salt has been made the subject of an exhaustive study by Young, Mitchell, and Burke (*J. Amer. Chem. Soc.*, 1904, **26**, 1389, 1413), and by Young and Burke (*ibid.*, 1906, **28**, 315). These authors have shown the existence of twelve different solid hydrates, besides the anhydride, have determined their compositions, solubilities, transition points, and the conditions under which they are formed. They seem to

FIG. 2.



have worked almost entirely with the fused pentahydrate; in a few cases certain hydrates are said to crystallise from solutions of different concentrations, but further particulars are not given. Moreover, their crystallisations were produced from solutions kept at rest, and the effect of mechanical friction does not appear to have been tried. •

In the present investigation, solutions of widely different concentrations have been used; they have been cooled slowly with constant shaking as in previous work, and mechanical friction has been brought into play by introducing angular fragments of Jena glass before sealing. The supersolubility curves for ice and the secondary monohydrate (Young and Burke's nomenclature is used) have been traced, both these solid phases giving well-defined metastable regions. The more concentrated solutions were prepared by sealing up weighed quantities of the anhydride, the stable form above 70°, and distilled water in glass tubes; the dilute solutions were made up from pure recrystallised primary (ordinary) pentahydrate. To remove all traces of crystalline nuclei from the more

concentrated solutions, it was necessary to heat the tubes for some time—generally about an hour—in an oil-bath to a temperature of about 180°. The less concentrated tubes were heated in boiling water.

Crystallisation of Ice.—On cooling solutions of sodium thio-sulphate of concentrations from zero to about 40 parts per 100 of water with constant shaking, ice separates out at a definite temperature for each concentration. Table V gives the highest temperatures of spontaneous crystallisation of ice from solutions of varying strengths.

TABLE V.

(The tube contained 2·4 to 5·2 grams of solution.)

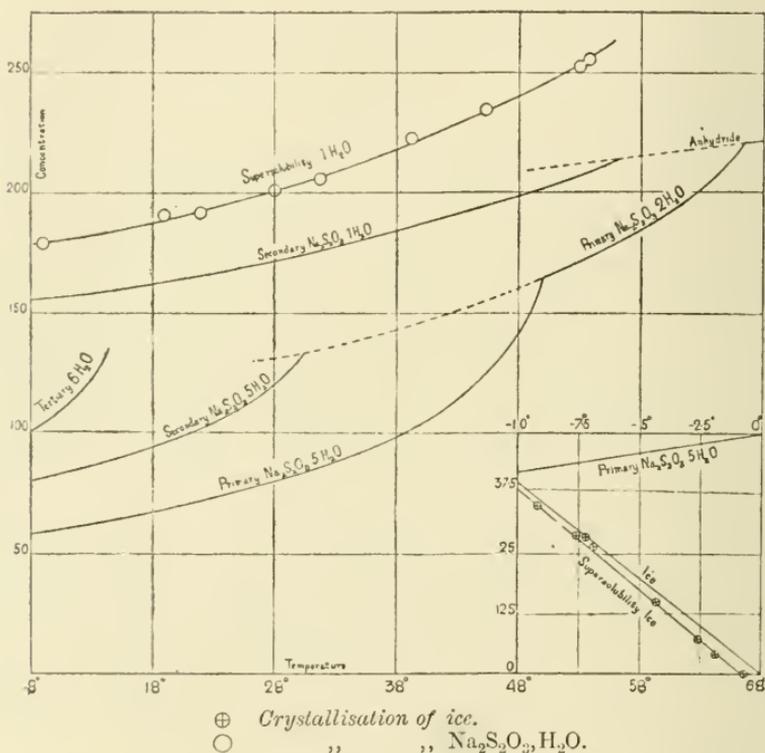
Parts of $\text{Na}_2\text{S}_2\text{O}_3$ in 100 parts H_2O ...	0·0	4·01	7·13	14·94	26·44	28·75	28·96	35·31
Temp. of crystal- lisation of ice ...	-0·7°	-1·9°	-2·6°	-4·3°	-6·9°	-7·2°	-7·6°	-9·2°

The formation of the ice crystals was a very definite phenomenon. Successive determinations with the same tube generally agreed within one or two tenths of a degree. The data are plotted on the diagram inset in Fig. 3, the scale for the ice-curves being double that of the rest of the diagram. The temperatures of spontaneous crystallisation are seen to lie on a regular supersolubility curve running nearly parallel to the freezing-point curve at a distance from it of from three-quarters to one-half a degree, and gradually approaching it with increasing concentration. The curve was not carried further, owing to the inconvenience of working with lower temperatures; the average temperature of the laboratory was about 30°, rising at times above 40°. Moreover, there were indications that with increasing concentration the solutions tended to become sluggish, and not to crystallise at all within a reasonable time. A solution of concentration 47·67 did not crystallise at -13°, although expected to give ice at -11°, and solutions of concentrations 79·98 and 80·67 did not crystallise at -15°.

Crystallisation of $\text{Na}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (secondary).—When solutions of sodium thiosulphate of concentrations between 178 and 255 were slowly cooled and shaken in sealed tubes containing glass fragments, this solid phase invariably crystallised out. At a definite temperature for each tube, a shower of crystals appeared, causing a milky appearance in the tube. The crystals were identified as those of the secondary monohydrate by determinations of their solubility. In the case of the more concentrated solutions, which crystallised spontaneously between 30° and 55°, the phenomenon was very definite. Crystallisation always took place after being kept at a certain maximum temperature with constant shaking for

ten minutes or a quarter of an hour. Successive determinations with the same tube agreed to within half a degree. In the more dilute solutions, which crystallised at lower temperatures, 5° to 30° , the crystallisation was somewhat less definite, a rather longer time being necessary to insure crystallisation. Crystallisation would, however, always occur after standing half an hour to an hour at the maximum temperature. The greater length of time required was due to the greatly increased viscosity of the solutions at these temperatures. At still lower temperatures, the viscosity

FIG. 3.



became too great to allow of crystallisation taking place within a reasonable time. The solutions, indeed, became so viscid that they could neither be shaken nor poured. Such solutions were therefore unsuitable for determining a supersolubility curve. They would in general only crystallise after standing for protracted periods, amounting often to weeks or months. In such cases, it was not the monohydrate which separated out, but one of the other possible solid phases, generally the dihydrate or secondary pentahydrate. Between the concentrations 178 and 255, however, it was always the monohydrate which appeared on slow cooling, so long as the

tube was constantly shaken. Table VI gives the highest temperatures at which spontaneous crystallisation was observed in such tubes.

TABLE VI.

(The tube contained from 2.2 to 8.4 grams of solution.)

Parts of $\text{Na}_2\text{S}_2\text{O}_3$ in 100 parts H_2O :	178.99	190.43	191.60	201.13	205.88	222.73	234.62	253.00	255.23
Temp. of crystallisation of $\text{Na}_2\text{S}_2\text{O}_3, \text{H}_2\text{O}$:	9.0°	18.9°	21.9°	28.0°	31.7°	39.2°	45.3°	52.9°	53.7°

The results are plotted in Fig. 3, and give rise to a regular supersolubility curve running roughly parallel to the solubility curve at a distance of about 20° from it. For the sake of clearness in the figure, only the solubility curves of the more important hydrates have been shown.

If the tubes were not shaken constantly during cooling, it was not always the monohydrate which crystallised. In the tube of concentration 234.6, on one occasion, crystals of the anhydride were formed when the tube was allowed to cool slowly without shaking from 50° . This was the only occasion on which the anhydride was produced spontaneously. It is possible that nuclei of the anhydride may have been left in the tube, although its previous treatment renders this unlikely. The dihydrate crystallised out in the tubes of concentrations 191.6 and 201.1 when they were kept at rest at the ordinary temperature, and was identified by its solubility.

Owing to the viscosity of the solutions, and the long times necessary for crystallisation for concentrations between about 50 and 170, no systematic investigation of the spontaneous crystallisation of such solutions was made.

Tubes containing 47.67, 79.99, 80.67, 146.39, and 153.38 parts of $\text{Na}_2\text{S}_2\text{O}_3$ respectively to 100 parts of water did not crystallise after keeping for some months at the ordinary temperature or after a short time at about -10° to -15° .

Tubes containing 124.09, 145.31, 162.58, 166.83, and 169.94 parts of $\text{Na}_2\text{S}_2\text{O}_3$ to 100 parts of water gave secondary pentahydrate on exposure to temperatures of about -8° to -15° after standing some hours.

The spontaneous formation of the primary (ordinary) pentahydrate was observed in two tubes only. These had concentrations of 100.7 and 101.1, and were the first two tubes prepared. Since they had shown themselves to be unsuited for the determination of a supersolubility curve, they had been set aside and maintained at the laboratory temperature without being kept under close

observation. On examination five months after, both tubes were found to contain large, transparent, glassy crystals. Determination of their solubility showed them to be the ordinary pentahydrate. This was confirmed by the fact that on warming there was no sign of any change into a different hydrate, as would probably have occurred with any other hydrate heated to the same temperature, 39° to 40° . Moreover, after having dissolved the crystals until only a small fragment remained, and then allowing to cool slowly with shaking, a shower of brilliant little monoclinic prisms was obtained identical in appearance with the ordinary pentahydrate. According to Young and Burke, the spontaneous production of this solid phase was never observed in solutions or fusions of sodium thiosulphate. They found, however, that it was produced from all the other solid hydrates by exposure to a temperature of -35° . It is noteworthy that in the only two cases in which the spontaneous formation of this phase has been observed, the concentrations were nearly the same—100.7 and 101.1—and it would seem, therefore, that at such concentrations the dissolved salt was in the most favourable condition to form this hydrate. It is certain that in the tubes under discussion no solid nuclei of the pentahydrate were present. For in spite of having been cooled to low temperatures, no crystallisation of this hydrate was observed during the space of a week; and it is probable that no crystallisation took place before some months of standing.

Summary.

1. Supersaturated solutions of sodium carbonate, freed from crystal nuclei, crystallise at definite temperatures on being subjected to mechanical friction.

2. Supersolubility curves have been traced showing the conditions under which ice, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, and $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ are formed spontaneously from sodium carbonate solutions.

3. Contrary to Ostwald's law of successive reactions, the less stable $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$ is only rarely produced spontaneously. The conditions favouring the spontaneous formation of this phase appear to exist only in solutions of concentrations between certain narrow limits. In such solutions, however, the tendency to produce the decahydrate appears to be equally well marked.

4. Supersaturated solutions of sodium thiosulphate, freed from crystal nuclei and between certain limits of concentration (0 to 40 and 179 to 255 parts of anhydrous salt to 100 parts of water), crystallise at definite temperatures when subjected to mechanical friction.

5. Supersolubility curves have been traced showing the conditions

under which ice and $\text{Na}_2\text{S}_2\text{O}_3, \text{H}_2\text{O}$ (secondary) crystallise spontaneously from solutions of sodium thiosulphate.

6. Under the conditions employed—slow cooling and constant shaking—ice and $\text{Na}_2\text{S}_2\text{O}_3, \text{H}_2\text{O}$ are the only two of the fourteen possible solid phases which crystallise out spontaneously within the space of one or two hours.

7. The spontaneous production of anhydrous $\text{Na}_2\text{S}_2\text{O}_3$, primary $\text{Na}_2\text{S}_2\text{O}_3, 2\text{H}_2\text{O}$, secondary $\text{Na}_2\text{S}_2\text{O}_3, 5\text{H}_2\text{O}$, and ordinary (primary) $\text{Na}_2\text{S}_2\text{O}_3, 5\text{H}_2\text{O}$ has been observed in solutions of sodium thiosulphate kept at rest for longer periods. Owing to the viscosity of the solutions, and the long time necessary for crystallisation, it was not found practicable to trace any regular relationship between the temperature of crystallisation and the concentration of the solution.

GOVERNMENT COLLEGE,
LAHORE, INDIA.

CLXXXVI.—*The Iodobenzenemonosulphonic Acids. Part I.*

By MARY BOYLE.

ALTHOUGH a large number of chloro- and bromo-derivatives of benzenesulphonic acid and of the homologous acids have been prepared, little is known of the corresponding iodo-compounds, the *o*-, *m*-, and *p*-iodo-derivatives alone being known in the case of benzenesulphonic acid.

The investigation, of which the first part is described in this communication, has for its object the preparation and study of the higher iodo-derivatives of benzenesulphonic acid, and an account is given of 2:4-, 2:5-, 3:4-, and 3:5-di-iodo-, and 2:3:5-, 2:4:5-, and 3:4:5-tri-iodo-benzenesulphonic acids.

Historical.

p-Iodobenzenesulphonic acid was first described in 1872 by Körner and Paterno (*Gazzetta*, **2**, 448), who prepared it from iodobenzene and fuming sulphuric acid; it was subsequently prepared by Lenz in 1877 (*Ber.*, **10**, 1135) by displacing the amino-group of aniline-*p*-sulphonic acid by iodine.

The ortho-acid was prepared by Bahlmann in 1877 (*Annalen*, **186**, 325) by the action of fuming hydriodic acid on the diazo-salt of aniline-*o*-sulphonic acid; the meta-acid was prepared in like manner from aniline-*m*-sulphonic acid by Langmuir in 1895 (*Ber.*, **28**, 93). Iodo-derivatives of several sulphonic acids of the

homologues of benzene have also been prepared, namely, *o*-iodotoluenesulphonic acid by Mabery and Palmer (*Amer. Chem. J.*, 1884, **6**, 170); the para-derivative by Glassner (*Ber.*, 1875, **8**, 560) and de Roode (*Amer. Chem. J.*, 1891, **13**, 233); a disulphonic acid of *p*-iodotoluene by Richter (*Annalen*, 1885, **230**, 325); an iodoxylenesulphonic acid by Hammerich (*Ber.*, 1890, **23**, 1635); a di-iodoxylenesulphonic and an iodomesitylenesulphonic acid by Töhl (Töhl and Bauch, *Ber.*, 1893, **26**, 1107; Töhl and Eckel, *Ber.*, 1893, **26**, 1101), besides others of a more complex nature.

Theoretical.

The sulphonation of iodo-compounds in all cases involves the formation of compounds richer in iodine, the sulphuric acid acting to a certain extent as a carrier of halogen, and causing the transfer of iodine from one molecule to another. Such sulphonating experiments, therefore, result in the production of at least three substances, namely, (1) a compound containing more iodine in the nucleus than the original substance; (2) an iodosulphonic acid; (3) a sulphonic acid free from iodine, the molecule which has lost the iodine being, as a rule, readily attacked by the sulphonating agent. Such was observed to be the case by Hammerich (*loc. cit.*), who subjected iodo-*m*-xylene to the action of concentrated sulphuric acid, also by Neumann (*Annalen*, 1887, **241**, 47) during his investigation of the action of sulphuric acid on iodobenzene.

The latter observer studied the conditions under which sulphonation of the iodo-compound is possible, and arrived at the conclusion that strength of acid, proportions of the interacting substances, and temperature are all important factors to be taken into consideration. As a rule, concentrated acid favours sulphonation, high temperatures the production of di-iodobenzene.

My first attempts to prepare 2:5-di-iodobenzenesulphonic acid were made on the lines of these experiments, since it was evident that if *p*-iodoaniline or *p*-iodoacetanilide could be directly sulphonated, the conversion of either product into the required acid would be a matter of little difficulty. The results were very unsatisfactory.

In the case of iodoaniline hydrochloride, no sulphonation was effected at low temperatures, and, on gently heating the mixture, iodine was copiously evolved; in the case of iodoacetanilide, when the conditions were such as to render sulphonation possible, a considerable amount of iodine was evolved, and the sulphonic acid obtained did not contain the halogen.

It may be noted that similar results have been obtained with

iodophenolic compounds by Neumann (*loc. cit.*), his attempts to prepare an iodophenolsulphonic acid by direct sulphonation of the iodophenol having resulted, at the ordinary temperature, in the elimination of iodine, and, at low temperatures, in the formation of a di-iodo-derivative unaccompanied by any sulphonic acid.

The action of sulphonating agents on *p*-di-iodobenzene was next studied, but with not much more satisfactory results.

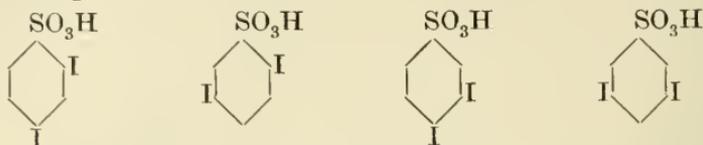
The di-iodobenzene was treated both with the calculated amount and with excess of concentrated sulphuric acid, with fuming acid of various strengths, and with sulphur trioxide at many different temperatures. At the ordinary temperature, no action took place with either concentrated or fuming acid; at the temperature of the water-bath, fuming acid caused the formation of tri- and tetra-iodobenzene and a trace of a sulphonic acid. The vapour of sulphur trioxide, when passed over dry and slightly warm di-iodobenzene, caused the formation of small quantities of the higher iodo-derivatives of benzene, but when the experiment was carried out at higher temperatures, the proportion of unchanged material became much less, and a small amount of a crystalline di-iodobenzenesulphonic acid was isolated.

The yield, however, was so extremely poor, being, under the most favourable conditions, less than 10 per cent., and becoming much less when large quantities were dealt with, that the method, as a means of preparing a large amount of the acid, was seen to be hopeless, and was abandoned.

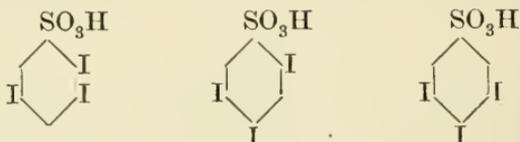
The possibility of introducing iodine into substances already containing a sulphonic group was next considered. A patent by Kalle and Co. (D.R.-P. 129808), describing the preparation of iodo-substituted derivatives of aniline-*m*- and -*p*-sulphonic acids, indicated that success in that direction had already been achieved. A brief description of the preparation of the iodo-derivatives of these acids is given in the patent, but, as far as can be gathered from a study of subsequent literature, they have not been investigated with a view to the determination of their structure; and others, prepared by myself, which form the starting point for the preparation of several iodobenzenesulphonic acids described in this paper, are not mentioned.

Of these sulphonic acids, 3:4-di-iodobenzenesulphonic acid, prepared from the monoiodoaniline-*p*-sulphonic acid described by Kalle and Co., which is readily obtained in large amount, was first studied; the preparation of 2:5-di-iodobenzenesulphonic acid, which involves the production of aniline-*o*-sulphonic acid, and is a more lengthy operation, was undertaken later.

Of the six theoretically possible di-iodobenzenesulphonic acids, the following four:



and, of the six theoretically possible tri-iodobenzenesulphonic acids, the following three:



have been prepared and examined by the author.

Only two of these acids, namely, 2:5- and 3:4-di-iodobenzenesulphonic acids, have been thoroughly investigated with regard to the properties of the acids, their derivatives and salts; derivatives and salts of the other acids have been prepared, but have not as yet been studied.

Indirectly, during the course of the work, several iodoanilinesulphonic acids, isomeric with that described by Kalle and Co., and some iodonitrobenzenesulphonic acids in the form of their potassium salts, have been prepared but not subjected to examination.

It is stated in the specification of the patent referred to that mono- and di-iodoaniline-*p*-sulphonic acids are produced from aniline-*p*-sulphonic acid by the action of one and two molecular proportions of iodine monochloride respectively, and that a di-iodoaniline-*m*-sulphonic acid is formed under very similar conditions. On carrying out experiments with aniline-*m*-sulphonic acid under the conditions described by Kalle and Co., the statement that a di-iodoacid is produced was confirmed, but it was found that under carefully regulated conditions a monoiodoaniline-*m*-sulphonic acid may also be prepared, and, as the constitution of this acid is readily determined, its formation is of service in the elucidation of the constitution of the more highly iodinated product. Judging from the results obtained with aniline-*m*- and -*p*-sulphonic acids, it was to be expected that aniline-*o*-sulphonic acid should also give rise to iodo-substituted derivatives; experiments in this direction have been attended with marked success, well-defined crystalline monoiodo- and di-iodo-aniline-*o*-sulphonic acids having been obtained.

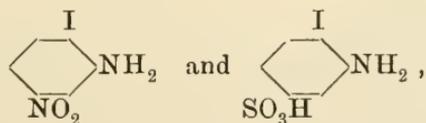
The constitutions of these six iodoanilinesulphonic acids are, in most cases, quite clear, and rigid proofs of structure have been obtained in the case of four of them.

Monoiodoaniline-p-sulphonic Acid.—In the case of monoiodo-

aniline-*p*-sulphonic acid, the formation of *m*-iodobenzenesulphonic acid (identified in the form of its amide) on the removal of the amino-group by the diazo-method, is proof that the iodine atom occupies the ortho-position with respect to the amino-group; consequently, the di-iodo-acid, obtained by directly displacing the amino-group by iodine, is 3:4-di-iodobenzenesulphonic acid.

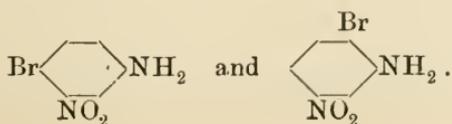
Monoiodoaniline-m-sulphonic Acid.—As this acid is convertible into a di-iodosulphonic acid identical with that obtained from monoiodoaniline-*p*-sulphonic acid, the ortho-position with respect to the amino- and the para-position with respect to the sulphonic group must be occupied by iodine, as 6-iodoaniline-*m*-sulphonic acid is alone capable of giving rise to 3:4-di-iodobenzenesulphonic acid. Recent work by Brenans (*Compt. rend.*, 1904, **138**, 1503; **139**, 63) and by Körner and Contardi (*Atti R. Accad. Lincei.*, 1908, [v], **17**, i, 465) on the iodination and bromination of *m*-nitroaniline is of interest in connexion with the iodination of aniline-*m*-sulphonic acid, inasmuch as it admits of a comparison being made between the influences exerted by the negative nitro- and sulphonic groups on the position assumed by the entering halogen atom. Brenans states that the action of iodine chloride on *m*-nitroaniline dissolved in acetic acid results in the production of 6-iodo-3-nitroaniline, 2:4-di-iodo-3-nitroaniline, and 2:6-di-iodo-3-nitroaniline.

That is to say, the first atom of iodine assumes the same position relatively to the amino- and nitro-groups as it does in aniline-*m*-sulphonic acid with respect to the amino- and sulphonic groups, thus:

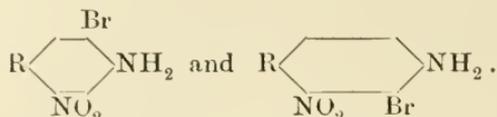


but the second atom of iodine seems (according to Brenans) to be as readily introduced into the second ortho-position as it is into that para- with respect to the amino-group; I find, however, in the case of aniline-*m*-sulphonic acid, that the second atom of iodine, as will be shown later, enters only into the para-position.

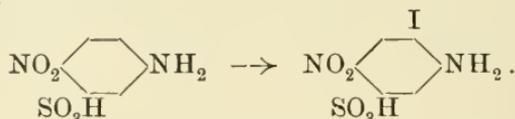
The results of Körner and Contardi's observations on the bromination of *m*-nitroaniline dissolved in acetic acid are not in harmony with the above, bromine entering into the para-position by preference, and only to a small extent into the ortho-position with respect to the amino-group, which is that assumed in the first instance by iodine, thus:



It is further stated that, if the para-position is occupied, the bromine atom enters either ortho-position indifferently, thus:



In the case of aniline-*m*-sulphonic acid, only one di-iodo-derivative has been isolated, and it has not yet been found possible to displace the hydrogen in the position between the amino- and sulphonic groups by the halogen, so that there is an essential difference between the nitro- and sulphonic groups as regards their directive influence, the latter in conjunction with the amino-group forming, as it were, a screen which prevents all interaction with the enclosed hydrogen atom. The impregnability of this second ortho-position was clearly manifested in an experiment with *p*-nitroaniline-*m*-sulphonic acid, a solution of which, in very dilute hydrochloric acid, was treated with a considerable excess of iodine chloride. It was thought that, as the para-position was occupied, the second atom of iodine would enter the second ortho-position, but under no conditions could a di-iodo-derivative of any kind be obtained, the monoiodo-compound of the following constitution being alone produced:



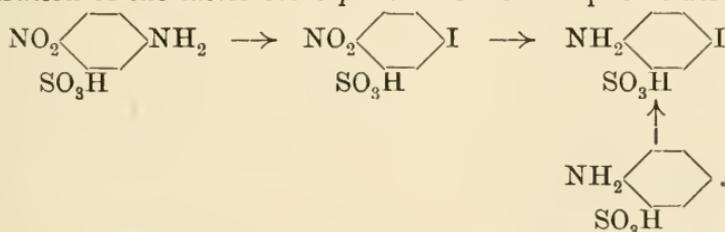
The failure to introduce iodine into this position and the non-formation of a tri-iodoaniline-*m*-sulphonic acid is the more remarkable in that a tribromoaniline-*m*-sulphonic acid has been obtained by Berndsen (*Annalen*, 1874, 174, 84) and by Reinke (*Annalen*, 1877, 186, 286) by the action of bromine on aniline-*m*-sulphonic acid. This failure may be due to the very sparing solubility of the di-iodo-acid, which is rapidly removed from the further action of the iodine chloride, but such a suggestion will not serve to explain the results obtained with *p*-nitroaniline-*m*-sulphonic acid which remained in solution throughout.

Monoiodoaniline-o-sulphonic Acid.—The action of iodine chloride on a solution of aniline-*o*-sulphonic acid gives an excellent yield of the monoiodo-derivative. Further action under specially regulated conditions which are discussed in the experimental part of this paper, gives rise to a di-iodo-derivative; under no conditions, as was to be expected, can a third iodine atom be introduced into the nucleus.

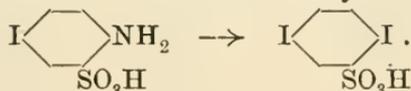
The monoiodoaniline-*o*-sulphonic acid is the pure para-compound,

free from any admixture of the ortho-isomeride; if produced at all, the latter must be present in such small amount as to escape detection; the second iodine atom enters the free ortho-position. That the iodine atoms occupy the positions stated has been clearly demonstrated. As it was clear that the iodine atom in the monoiodo-derivative was in either the para- or the ortho-position with respect to the amino-group, the displacement of the latter by hydrogen, leading, as it would, to *m*-iodobenzenesulphonic acid in both cases, could give no definite information as to the constitution of the acid. The amino-group was therefore displaced by iodine, and attempts were made to remove the sulphonic group and obtain a di-iodobenzene. These attempts, as might be expected, proved unsuccessful. The acid proved to be perfectly stable when heated in superheated steam; and when a mixture of the potassium salt with sulphuric acid was heated in the same way, although the sulphonic group was removed, the product became further iodinated in the presence of the sulphuric acid; tri- and tetra-iodobenzenes were isolated, but no trace of a di-iodobenzene could be detected.

Finally, the relative positions of the amino-group and the iodine atom in monoiodoaniline-*o*-sulphonic acid were demonstrated by the preparation of the latter from *p*-nitroaniline-*m*-sulphonic acid:



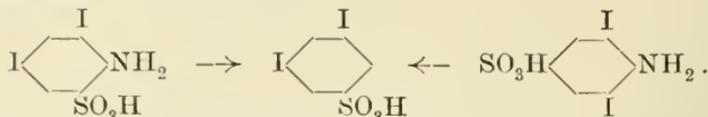
The constitution of the di-iodobenzenesulphonic acid prepared directly from this acid is therefore definitely settled:



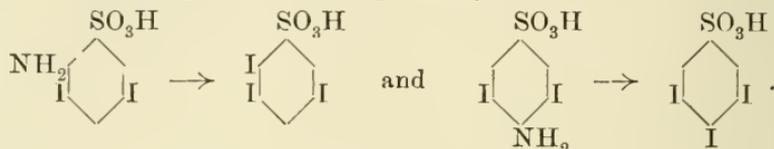
*Di-iodoaniline-*o*- and -*p*-sulphonic Acids.*—Although the monoiodo-derivatives of aniline-*o*- and -*p*-sulphonic acids may theoretically each give rise to three isomeric di-iodo-derivatives, taking into account the well-known fact that halogens always act on amino-compounds in such a manner that the halogen enters into either the ortho- or the para-position, the only two derivatives to be considered are the following:



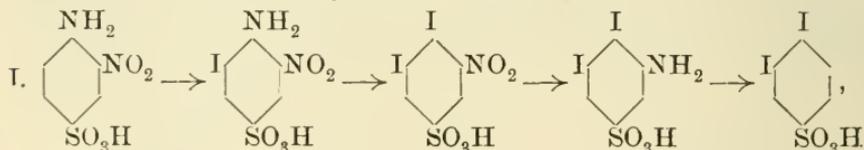
On displacement of the amino-group by hydrogen, these two acids should yield one and the same di-iodosulphonic acid; this was found actually to be the case:



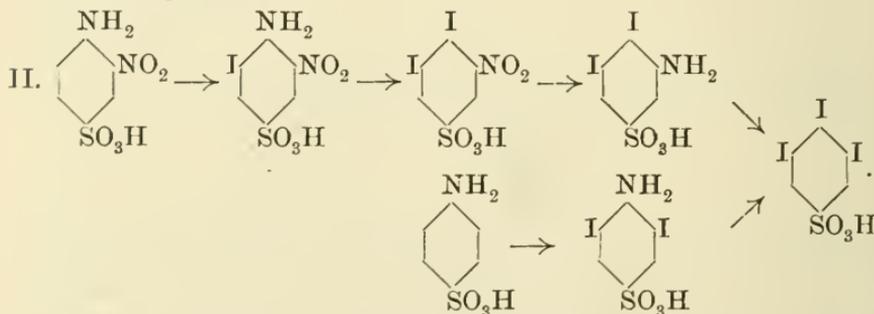
The two tri-iodo-acids prepared directly from these amino-acids must be therefore 2: 3: 5-tri-iodobenzenesulphonic acid and 3: 4: 5-tri-iodobenzenesulphonic acid respectively:



It was thought that independent confirmation of the position of the iodine atoms in the two di-iodoamino-acids would be afforded if the series of changes could be effected which is indicated in the two following schemes, the first having in view the determination of the position assumed by the first iodine atom:



the relative positions of the iodine atoms in the last acid being known; and the second, the proof of the constitution of 2: 6-di-iodoaniline-*p*-sulphonic acid:



If the tri-iodo-acid finally obtained, the constitution of which is definitely settled by the method of its production, is identical with the one obtained from di-iodoaniline-*p*-sulphonic acid, the constitution of the latter is also clear. An unexpected difficulty, however, arose in attempting to carry out the experiment. The nitroaniline-*p*-sulphonic acid readily absorbed iodine under the usual conditions, but when this iodo-derivative was diazotised and treated

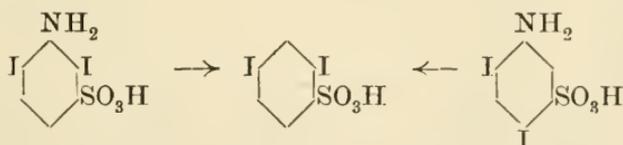
with potassium iodide, a crystalline potassium salt was obtained, which proved to be a salt, not of the expected di-iodonitrosulphonic acid, but of the tri-iodobenzenesulphonic acid of the second scheme, the nitro-group having been displaced by an iodine atom.

A similar displacement of a nitro-group by iodine was not observed in the case of the isomeric 4-nitroaniline-*m*-sulphonic acid, which exhibited normal behaviour throughout, so that it seems that the proximity to the nitro-group of the amino-group which is subjected to the action of nitrous acid, is an important factor in determining the nature of the interaction.

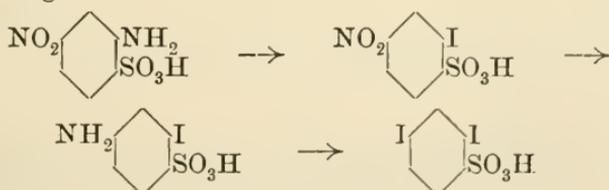
As regards the problem under consideration, although, owing to the abnormal character of the change, the result scarcely affords decisive proof, the formation of the tri-iodosulphonic acid from a monoiodo-derivative, in which the iodine is undoubtedly in the ortho-position with respect to the amino-, and in the meta-position with respect to each of two negative groups, is convincing evidence of the constitution of the acid.

Di-iodoaniline-m-sulphonic Acid.—That this acid is the 4:6-di-iodo-acid, and that the tri-iodo-acid formed from it is the 2:4:5-tri-iodo-acid, is quite clear from the following considerations.

1. The removal of the amino-group from di-iodoaniline-*m*-sulphonic acid involves the production of a di-iodobenzenesulphonic acid which, from other modes of preparation, must be regarded as 2:4-di-iodobenzenesulphonic acid. Two possible configurations of the amino-acid could give rise to this substance, namely:



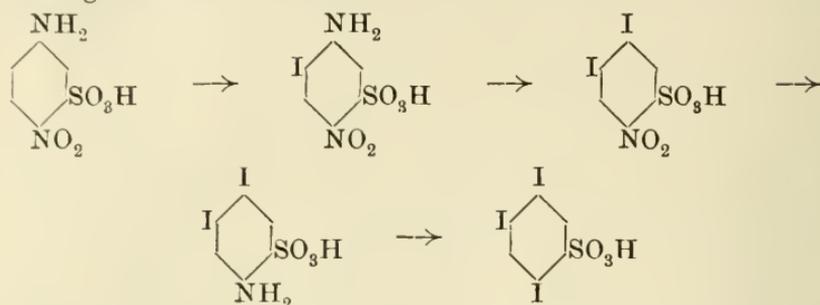
This di-iodo-acid can be prepared from 5-nitroaniline-*o*-sulphonic acid in such a way as to establish its constitution by the following series of changes:



One iodine atom in di-iodoaniline-*m*-sulphonic acid therefore occupies the para-, the second the ortho-position, with respect to the sulphonic group.

2. If 4-nitroaniline-*m*-sulphonic acid is treated with iodine chloride, it yields a monoiodo-derivative, from which a tri-iodo-acid

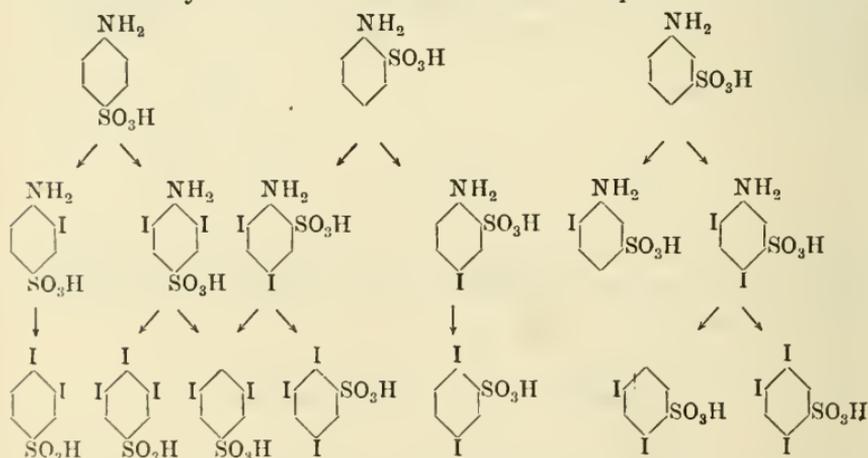
may be obtained by carrying out the changes expressed in the following scheme:



In this manner, the same tri-iodosulphonic acid is obtained as may be produced directly from di-iodoaniline-*m*-sulphonic acid. The constitution of the original nitroamino-acid requires that the tri-iodo-acid finally obtained shall possess two iodine atoms in para-positions with respect to each other.

Since, therefore, one iodine atom must be in the para-position with respect to the sulphonic group and two others in para-positions with respect to each other, the constitution of the tri-iodo-acid is settled beyond question as being 2:4:5-tri-iodobenzenesulphonic acid.

The following table shows at a glance how the seven acids under discussion may be obtained from the anilinesulphonic acids:



The iodobenzenesulphonic acids are all extremely soluble in water, much less so in mineral acids; they all crystallise well from mineral acid solutions; the 2:5-di-iodo- and the 2:4:5-tri-iodo-benzenesulphonic acids crystallise extremely well from water alone.

The chlorides crystallise in well-defined forms; the amides are white powders insoluble even in hot water, but, in the case of the tri-iodo-compounds, crystallise well from alcohol; the two anilides

which have been prepared can also be crystallised from alcohol. The acids are characterised by forming beautifully crystalline salts and esters.

The diazo-anhydrides of the iodoaminosulphonic acids considered in this paper are all coloured, the colour varying from the palest yellow, almost cream colour, in the case of *p*-iodoaniline-*o*-sulphonic acid, to bright yellow in the case of all the di-iodoamino-acids. They are only sparingly soluble in sulphuric acid, and are comparatively stable in the dry state.

Melting Points of the Acids and of their Derivatives.

Benzene-sulphonic acids.	Anhydrous acid.	Chloride.	Amide.	Ethyl ester.	Anilide.
3:4-Di-iodo	122—125°	82°	227°	81°	—
2:5-Di-iodo	132°	131—132°	211—230°	112·5°	—
3:5-Di-iodo	146	92·5	210—218	—	—
2:4-Di-iodo	167	78	230	—	—
3:4:5-Tri-iodo ..	211	145	above 250	—	201°
2:4:5-Tri-iodo ..	230	135	„ 288	155	194—196
2:3:5-Tri-iodo ..	210—215	122·5	„ 280	110	—

EXPERIMENTAL.

3:4-Di-iodobenzenesulphonic Acid.

The material used for preparing this acid is the monoiodoaniline-*p*-sulphonic acid described by Kalle and Co. (*loc. cit.*). 17·3 Grams of aniline-*p*-sulphonic acid are dissolved in about 2 litres of hot water, the solution cooled and mixed with 30 c.c. of concentrated hydrochloric acid; after cooling the mixture to about 10°, a molecular proportion of iodine chloride (16·3 grams) is drawn into it, the flask containing the chloride being heated on a water-bath kept at 70—80°, and the exit tube from the flask containing the acid solution being attached to the pump.

The dark brown mixture was kept for twelve hours, and then evaporated to crystallisation; the long, white needles which separated were purified by crystallisation from water. The yield of monoiodoaniline-*p*-sulphonic acid approximated to 50 per cent. of the theoretical:

Found, C = 23·84; H = 1·92; N = 4·71; I = 42·54.

C₆H₄O₃NIS requires C = 24·08; H = 2·00; N = 4·68;

I = 42·47 per cent.

Constitution of Monoiodoaniline-p-sulphonic Acid.—Although there could be little doubt that the iodine occupied the position ortho- with respect to the amino-, and meta- with respect to the sulphonic group, in order completely to verify the point, the amino-

group was displaced by hydrogen and the resulting *m*-iodobenzenesulphonic acid was converted into its amide and identified.

The displacement of the amino-group by hydrogen was effected by boiling the *diazo-anhydride* (Found, N=9.14. $C_6H_3O_3N_2IS$ requires N=9.03 per cent.) with methylated spirit or with 95 per cent. alcohol under a pressure slightly above the ordinary. Under the atmospheric pressure, using absolute alcohol, the amino-group was also partly displaced by the ethoxy-group. The flask containing the mixture was attached to a reflux condenser, and a tube bent twice at right angles was inserted through the tightly-fitting cork closing the top of the condenser; the whole length of the further limb of this tube, about 400 mm. long, was immersed in mercury (compare Schmitt, *Annalen*, 1861, **120**, 152; Ador and Meyer, *ibid.*, 1871, **159**, 10). After some time, a vigorous evolution of gas occurred and the diazo-compound passed into solution, a deep red colour being developed. On evaporating the liquid on the water-bath, a dark red, pasty mass remained; on diluting this slightly, and pouring it into a saturated solution of common salt, a copious, brownish-yellow precipitate of *sodium iodobenzene-m-sulphonate* was obtained. This salt was shaken with animal charcoal, and a portion further purified and freed from all traces of chloride by dissolving it in absolute alcohol:

Found, C=23.93; I=41.31.

$C_6H_4O_3ISNa$ requires C=23.53; I=41.50 per cent.

The purified salt was then treated with the requisite amount of phosphorus pentachloride, the liquid mixture heated for some time on the water-bath, and then added to concentrated ammonia. On gently warming, a voluminous, white precipitate was obtained, which, after crystallisation from water, separated in needles melting at 150—151°. The recorded melting point of iodobenzene-*m*-sulphonamide is 151—152°. The original amino-acid was thus proved to be *o*-iodoaniline-*p*-sulphonic acid.

To prepare 3:4-di-iodobenzenesulphonic acid, a solution of 20 grams of *o*-iodoaniline-*p*-sulphonic acid was rendered faintly alkaline with sodium carbonate, and mixed with 4.7 grams of sodium nitrite; the mixture was then poured gradually into 300 c.c. of dilute sulphuric acid cooled to 2°.

After about three hours, 15 grams of potassium iodide were added, and the mixture heated on the water-bath until all the nitrogen was evolved, and a clear red solution was obtained. Practically no evolution of gas took place below 15°; at that point vigorous effervescence began, the diazo-compound passing rapidly into solution.

In many experiments, when crude iodoaniline-*p*-sulphonic acid

was employed, and a slight excess of iodine chloride had been used in its preparation, fine, sparkling crystals made their appearance at this stage even in the hot solution; these, on examination, proved to be potassium 3:4:5-tri-iodobenzenesulphonate, a salt which is almost insoluble in water and is readily formed from di-iodoaniline-*p*-sulphonic acid by displacement of the amino-group by iodine.

This acid and its derivatives are described on p. 1711.

When pure recrystallised iodoaniline-*p*-sulphonic acid was used, no crystals separated until the red solution had been considerably concentrated; on cooling, a mass of glistening, pale yellow crystals separated, which became colourless on recrystallisation, crystallising from water in small needles and from alcohol in shining scales. Concentration of the mother liquor yielded a further crop of the same crystals, which proved to be *potassium 3:4-di-iodobenzene-sulphonate*. The yield of potassium salt was in some cases 70 per cent. of the theoretical:

Anhydrous salt: Found, I=56·39; K=8·58.

$C_6H_3O_3I_2SK$ requires I=56·69; K=8·70 per cent.

Hydrated salt: Found, C=15·55; H=1·01.

$C_6H_3O_3I_2SK, H_2O$ requires C=15·45; H=1·07 per cent.

3:4-Di-iodobenzenesulphonic acid was prepared from the potassium salt by converting the latter into the barium salt, and decomposing this with excess of dilute sulphuric acid; the acid solution was evaporated on the water-bath until, on cooling, masses of shining flakes separated. These were collected, dissolved in a little water, and precipitated with concentrated hydrochloric acid. The white crystals obtained were washed free from sulphuric acid with concentrated hydrochloric acid, dried on a porous plate, and freed from hydrochloric acid in a desiccator containing potassium hydroxide.

3:4-Di-iodobenzenesulphonic acid is a white, crystalline substance, extremely soluble in water, but is precipitated from the aqueous solution by acids. It does not crystallise well from water, attempts to purify it in this way giving a paste which filters extremely slowly, and, when pressed on a porous plate and left in the desiccator, dries to a hard cake. The dry acid is soluble in ether, and, when recovered from ether or when precipitated from a solution by hydrochloric acid, is extremely deliquescent. The crystals obtained from water, when dried in the air on a porous plate, melt irregularly from 80° onwards; when dried at 100° they melt at 122—125°; if the dried acid is once more exposed to moist air for a short time, the melting point is rapidly lowered to 80°.

There is no doubt, therefore, that the acid contains water of

crystallisation; the actual number of molecules has not yet been determined, owing to the difficulty of obtaining it in a sufficiently defined crystalline form.

Analysis of a specimen dried on porous plate in the desiccator seems to point to one molecule of water of crystallisation, but as there is every probability that partial dehydration had occurred, the point must be left undecided for the present:

Found, C=16.69; I=58.75.

$C_6H_4O_3I_2S, H_2O$ requires C=16.82; I=59.34 per cent.

Salts of 3:4-Di-iodobenzenesulphonic Acid.—The salts of this acid crystallise well from water. Many have been prepared, but of these only the sodium, barium, and lead salts have been thoroughly investigated with regard to their solubility and water of crystallisation; it is proposed to study the others similarly, and to communicate the results in a later paper.

Sodium 3:4-Di-iodobenzenesulphonate.—This salt was prepared from the pure acid by neutralisation with sodium hydroxide and recrystallisation from water. It crystallises in beautiful, white, glistening plates. For the determination of the water of crystallisation, the pure air-dried salt was heated to 160°:

Hydrated salt: Found, Na=5.05; H_2O =3.95.

$C_6H_3O_3I_2SNa, H_2O$ requires Na=5.11; H_2O =4.00 per cent.

Anhydrous salt: Found, C=16.82; H=0.93; I=59.28; Na=5.18.

$C_6H_3O_3I_2SNa$ requires C=16.66; H=0.69; I=58.79;
Na=5.32 per cent.

Solubility.—One hundred grams of water dissolve 3.47 grams of the anhydrous salt at 22.5°.

Barium 3:4-Di-iodobenzenesulphonate.—The barium salt was prepared from the pure acid by neutralisation with barium carbonate, and also by precipitation from the ammonium salt.

It crystallises in very small, white needles containing one molecule of water of crystallisation. For the determination of the water, about 1 gram of material was heated during several hours at 125°, two hours at 135°, and finally three hours at 140°; heating at 155° during another hour caused no further decrease in weight, but, on raising the temperature to 210°, decomposition, accompanied by darkening and considerable loss in weight, occurred:

Found, I=52.44; Ba=13.58; H_2O =1.68.

$C_{12}H_6O_6I_4S_2Ba, H_2O$ requires I=52.20; Ba=13.65;
 H_2O =1.84 per cent.

Solubility.—One hundred grams of water dissolve 0.27 gram of the anhydrous salt at 21.5°.

Lead 3:4-Di-iodobenzenesulphonate.—The lead salt separates

from water in very fine, white needles containing two molecules of water of crystallisation. The water was determined at two different temperatures, 170° and 250°, but identical results were obtained in the two cases:

Found, C=13·72; H=0·85; H₂O=3·38.

C₁₂H₆O₆I₄S₂Pb, 2H₂O requires C=13·57; H=0·94; H₂O=3·50 per cent.

Ammonium Salt.—This salt is extremely soluble in water, and it was not possible to obtain it in a crystalline condition.

Silver Salt.—This was obtained by precipitation from the ammonium salt; it crystallises from water in transparent needles, and darkens on exposure to light.

The nickel, cobalt, manganese, cerium and copper salts have all been prepared in small amount by precipitation from a fairly concentrated solution of the ammonium salt; they may be described roughly as follows.

Nickel salt: beautiful, long, green plates; *cobalt salt*: long, flat, pink crystals; *manganese salt*: small, white, sparkling crystals; *cerium salt*: thick, white nodules; *copper salt*: small, blue plates.

3: 4-*Di-iodobenzenesulphonyl Chloride*.—The chloride was prepared in some cases from the dry potassium salt, in others from the pure anhydrous acid by the action of phosphorus pentachloride. The potassium salt (5·3 grams) and phosphorus pentachloride (2·8 grams) were mixed, and heated on a water-bath during one hour. After cooling, water was added gradually, and, after one hour, the chloride was isolated by extraction with ether. Small, transparent needles, in many cases white nodules, separated, which, when recrystallised from ether, or, better, from a mixture of equal parts of benzene and light petroleum, separated in very long, transparent needles, melting at 82°, which, however, became white and opaque when left in the desiccator over sulphuric acid:

Found, C=17·11; H=0·83.

C₆H₃O₂ClI₂S requires C=16·80; H=0·74 per cent.

3: 4-*Di-iodobenzenesulphonamide*.—The amide was prepared from the crude chloride by adding it gradually to excess of cooled, concentrated ammonia, a white mass being at once precipitated. This was collected and well washed with cold water. It is insoluble in cold, and only sparingly soluble in hot, water, but is readily soluble in alcohol, from which, however, no separation of crystals takes place. For purification, it was either dissolved in 95 per cent. alcohol, and a few drops of water added to the warm solution until a turbidity was produced, or boiled repeatedly with water. It is a fine, white powder, which burns with a luminous, smoky flame, giving off iodine, and evolves alkaline fumes when heated with sodium hydroxide. Its melting point is 227°:

Found, C=17.56; H=1.28; I=62.13.

$C_6H_5O_2NI_2S$ requires C=17.60; H=1.22; I=62.10 per cent.

Ethyl 3:4-Di-iodobenzenesulphonate.—This was prepared by warming the sulphonyl chloride with twice its volume of absolute alcohol in the presence of excess of sodium hydroxide. On cooling, the mass was extracted with ether, and the ethereal solution, on evaporation, left white needles, melting at 81°.

2:5-Di-iodobenzenesulphonic Acid.

To obtain this acid, aniline-*o*-sulphonic acid was prepared by sulphonating *p*-bromoacetanilide with concentrated sulphuric acid (Kreis, *Annalen*, 1895, **286**, 377), and then removing the bromine by means of zinc dust and sodium hydroxide. It may be mentioned, however, that six hours' boiling with these agents, the time prescribed, was in all cases totally insufficient to reduce the bromo-compound.

As the strongly alkaline liquid was found to attack Jena flasks, a large open porcelain dish was used and the water renewed at intervals, boiling being continued during ten to eleven hours. Excellent yields of the acid in the form of grey, rhombic crystals were obtained in this way.

*Action of Iodine Chloride on Aniline-*o*-sulphonic Acid.*—The iodine chloride was passed into the solution of the acid under conditions very similar to those adopted in the corresponding experiments with aniline-*p*-sulphonic acid. It is essential to use a dilute solution of the acid in preparing the pure iodo-compound.

17.3 Grams of aniline-*o*-sulphonic acid were dissolved in about 1.75 litres of warm water. After cooling, 30 c.c. of concentrated hydrochloric acid were added, the solution cooled to 10°, and 16.3 grams of iodine chloride drawn through as in earlier experiments. From the reddish-violet solution, silky, grey crystals slowly separated; by the end of the experiment, a semi-solid mass was obtained.

After several hours, the crystals were collected and well washed with water. On concentrating the mother liquor, more crystals were obtained, but accompanied by beautiful, long, violet needles, which were very heavy, and could be separated to some extent mechanically from the grey plates; they consisted of di-iodo-aniline-*o*-sulphonic acid, a product which accompanies the mono-iodo-compound to a very slight extent under every condition so far tried.

In one experiment, when 4 grams in excess of the theoretical quantity of iodine chloride had been passed into the solution of the amino acid, about 1.5 grams of these purple needles were extracted

in a fairly pure condition from the final mother liquor; analysis pointed to a slight admixture of the monoiodo-derivative:

Found, C=17.67; H=1.41; I=59.09.

$C_6H_5O_3NI_2S$ requires C=16.94; H=1.17; I=59.76 per cent.

Iodoaniline-o-sulphonic acid crystallises in shining plates from much hot water; it is almost insoluble in cold water. It is noteworthy that the colour of the crystals varies in a rather arbitrary way, being sometimes buff, often very pale violet, but usually of a dull grey colour; it has not been found possible to determine what conditions favour the production of any particular coloured variety, but there is no doubt of the identity of the differently coloured substances:

Found, C=24.35; H=2.08; I=42.41.

$C_6H_6O_3NIS$ requires C=24.08; H=2.00; I=42.47 per cent.

The yield of pure iodoaniline-*o*-sulphonic acid amounted to 91 per cent. of the theoretical.

Constitution of Iodoaniline-o-sulphonic Acid.—It was pointed out in the theoretical part of this paper that attempts to remove the sulphonic group from the di-iodo-acid obtained from the iodoamino-acid by displacement of the amino-group by iodine were all unsuccessful, and that the relative positions of the iodo- and amino- or of the two iodo-groups were finally demonstrated by the preparation of the substance under investigation from a nitroamino-compound containing these two groups in the para-positions with respect to each other.

The attempts to remove the sulphonic group consisted in distilling either the dry acid or a mixture of its potassium salt with sulphuric acid in superheated steam; a third method consisting in heating a mixture of the acid with concentrated hydriodic acid in sealed tubes to 170°. In the first experiment, the unchanged acid was recovered intact; in the second, iodine was evolved, and tri- and tetra-iodobenzenes were separated from the distillate; in the third, very little action took place, the white solid, which separated from water and melted irregularly from 80° to 130°, being produced in too small quantities for accurate investigation. (*p*-Di-iodobenzene melts at 129°.)

The *p*-nitroaniline-*m*-sulphonic acid necessary for the determination of the constitution of iodoaniline-*o*-sulphonic acid was prepared from aniline-*m*-sulphonic acid by Eger's method (*Ber.*, 1888, **21**, 2581), by acetylating the barium salt and nitrating the crude product with a mixture of nitric and sulphuric acids. A yield corresponding with 56 per cent. of the aniline-*m*-sulphonic acid was finally obtained.

Conversion of p-Nitroaniline-m-sulphonic Acid into 5-Iodo-
VOL. XCV.

2-nitrobenzenesulphonic Acid.—The amino-compound (1.8 grams) was dissolved in warm water, together with a little sodium carbonate. The clear solution was poured into about 200 c.c. of dilute sulphuric acid, and the mixture cooled to 0°. One gram of sodium nitrite dissolved in water was then added gradually, when a yellow diazo-compound slowly separated. After the addition of a solution of 5 grams of potassium iodide, the mixture was warmed on the water-bath until the evolution of nitrogen was at an end.

On cooling the concentrated solution, *potassium 5-iodo-2-nitrobenzenesulphonate* separated in yellow plates. The yield was theoretical. The corresponding acid has so far been only very cursorily examined; its chloride and amide have been prepared, but no analyses have been made.

Conversion of 5-Iodo-2-nitrobenzenesulphonic Acid into p-Iodoaniline-o-sulphonic Acid.—It was anticipated that difficulty would be experienced in reducing the nitro-group without at the same time displacing iodine from the nucleus; in point of fact, in many experiments, the two actions proceeded simultaneously, a mixture of the amino- and of the iodoamino-compounds being obtained. The method eventually used was that described by Claisen and Thompson (*Ber.*, 1879, **12**, 1946), which consists in reducing the barium salt of the acid with the requisite amount of ferrous sulphate in the presence of barium hydroxide. It was found, however, to be more convenient to use the potassium salt of the idonitrosulphonic acid, and to reduce this by means of ferrous sulphate and potassium hydroxide. The nitro-group was reduced almost quantitatively, the iodine being unaffected. Curiously enough, in one experiment, when the barium salt was digested with ferrous sulphate and barium hydroxide, not only was the nitro-group reduced, but the iodine was also displaced.

Five grams of the potassium salt were dissolved in hot water, and the solution was mixed with 22 grams of crystallised ferrous sulphate dissolved in about 250 c.c. of water; the mixture was then heated on the water-bath, and a solution of 8.9 grams of potassium hydroxide was added. The black precipitate, which first formed, was gradually oxidised to the red hydrated ferric oxide; after two hours' heating on the water-bath and a few minutes over an ordinary flame, reduction was complete. Concentrated hydrochloric acid precipitated from the filtered solution a mass of grey crystals of *p*-iodoaniline-*o*-sulphonic acid. This acid was identified with that obtained by the action of iodine chloride on aniline-*o*-sulphonic acid by displacing the amino-group in both acids by iodine, and comparing the melting point of the *p*-di-iodosulphonic acid produced from the former, and also that of its chloride with

similar compounds formed from the latter acid. The melting points of the two acids were identical ($130\text{--}131^\circ$), as were also those of the chlorides ($131\text{--}132^\circ$), so that there is no doubt that when iodine chloride is passed into a solution of aniline-*o*-sulphonic acid, iodine enters into the para-position with respect to the amino-group:



2: 5-Di-iodobenzenesulphonic acid was prepared in the usual way from *p*-iodoaniline-*o*-sulphonic acid by the diazo-process. Unlike the other iodoaminosulphonic acids, which yield bright yellow diazo-compounds, this acid gives rise to a greyish-white or purplish-white substance, differing very slightly in appearance from the original amino-compound.

After adding potassium iodide, the reddish-yellow liquid was evaporated to crystallisation; on cooling, potassium 2: 5-di-iodobenzenesulphonate separated in golden-yellow needles which became cream-coloured on recrystallisation. The yield of potassium salt amounted to 84 per cent. of the theoretical. Again, as in the case of iodoaniline-*p*-sulphonic acid, when excess of iodine chloride is passed into the ortho-acid and no care taken to purify the resulting iodoaminosulphonic acid, diazotisation involves the production of a mixture of the potassium salts of the di-iodo- and tri-iodo-sulphonic acids; it is not difficult to separate the two, the latter being practically insoluble in cold, and very sparingly soluble in hot, water. These potassium salts were recrystallised and dried at 110° for analysis:

Potassium 2: 5-Di-iodobenzenesulphonate:

Found, C=16.07; H=0.67.

$\text{C}_6\text{H}_3\text{O}_3\text{I}_2\text{SK}$ requires C=16.07; H=0.67 per cent.

Potassium Tri-iodobenzenesulphonate: Found, C=12.48.

$\text{C}_6\text{H}_2\text{O}_3\text{I}_3\text{SK}$ requires C=12.54 per cent.

When a solution of potassium 2: 5-di-iodobenzenesulphonate is mixed with lead acetate, silver nitrate, or barium chloride, thick, white precipitates of the lead, silver, and barium salts are respectively produced. The acid was prepared by boiling the barium salt with a slight excess of dilute sulphuric acid; on evaporation of the filtrate, radiating masses of the acid were obtained in theoretical yield.

2: 5-Di-iodobenzenesulphonic acid crystallises in the above way from water containing a little sulphuric acid; from water alone, it crystallises in colourless, transparent plates, which become white

and opaque when left in the desiccator over sulphuric acid. Of the di-iodosulphonic acids prepared, this is the only one that separates from water in well-defined crystals. The crystals appear to contain water of crystallisation, for the air-dried substance begins to melt at about 80° , but the fusion is not complete until above 100° , whilst, when dried at 95 — 100° , the melting point is 132° . Further, when dried for some days at 100° , or for a shorter time at 130° , the material melts approximately at 195° . It is clear, then, that the acid melting at 80° contains water of crystallisation; that either this water is lost partly at 100° and completely at 130° , or that it is lost completely at 100° , and the high melting point of 195° is due to partial decomposition, or more probably to the formation of an anhydride. The correctness of the latter view has been manifested by the preparation of the anhydride, by treating the acid either with an excess of phosphorus pentachloride or with a mixture of this and phosphoryl chloride. It is a white substance, which melts irregularly at 235 — 245° . On exposure of the anhydrous acid to air, hydration rapidly occurs, with a consequent lowering of the melting point to 80° . On analysis:

Air-dried material, melting at 80° :

Found, C = 15.53; H = 2.36; H_2O = 11.88.

$C_6H_4O_3I_2S \cdot 3H_2O$ requires C = 15.51; H = 2.15; H_2O = 11.63 per cent.

Acid dried in desiccator over sulphuric acid:

Found, C = 17.03; H = 1.84.

Acid melting at 132° : Found, C = 17.25; H = 1.40.

Acid heated during several hours at 130° :

Found, C = 17.76; H = 1.02.

$C_6H_4O_3I_2S$ requires C = 17.56; H = 0.87 per cent.

The water of crystallisation was determined (1) by noting the loss in weight after application of heat; (2) by neutralising the acid with standard sodium hydroxide.

2: 5-Di-iodobenzenesulphonic acid dissolves very readily in water, moderately in ether, and is almost insoluble in mineral acids. Its salts all crystallise well.

Sodium 2: 5-di-iodobenzenesulphonate crystallises from water in cream-coloured plates, which are anhydrous:

Found, Na = 5.21.

$C_6H_3O_3I_2SNa$ requires Na = 5.32 per cent.

Solubility.—One hundred grams of water dissolve 6.82 grams of the salt at 22.5° .

Lead 2: 5-di-iodobenzenesulphonate crystallises in clusters of white, feathery needles. No absolutely satisfactory determinations of the water of crystallisation have been made; heating at 147°

during two hours caused a loss in weight corresponding with four molecules, but on heating to 200°, further loss, which may possibly be due to slight decomposition, occurred:

Found, $H_2O = 6.58$.

$C_{12}H_6O_6I_4S_2Pb, 4H_2O$ requires $H_2O = 6.56$ per cent.

Solubility.—One hundred grams of water dissolve 0.77 gram of the anhydrous salt at 20°.

Ammonium 2: 5-di-iodobenzenesulphonate is at once precipitated on the addition of ammonia to a solution of the acid; on recrystallisation, it separates in long, cream-coloured needles. A comparison of the ammonium salts of the 3:4-di-iodo- and the 2:5-di-iodosulphonic acids shows that the two differ enormously in solubility, the former being so soluble that it is impossible to isolate any crystals from the aqueous solution, the latter being even less soluble than the sodium salt.

Solubility.—One hundred grams of water at 20° dissolve 4.35 grams of the salt.

Barium 2: 5-di-iodobenzenesulphonate crystallises from much water in long, transparent needles, containing $4\frac{1}{2}$ molecules of water of crystallisation. The salt may be dehydrated by heating to 170°:

Found, $Ba = 13.20$; $H_2O = 7.69$.

$C_{12}H_6O_6I_4S_2Ba, 4\frac{1}{2}H_2O$ requires $Ba = 13.22$; $H_2O = 7.81$ per cent.

Solubility.—One hundred grams of water at 20° dissolve 0.522 gram of the anhydrous salt.

Potassium 2: 5-di-iodobenzenesulphonate crystallises in long, colourless needles, containing one molecule of water of crystallisation:

Found, $C = 15.36$; $H = 1.36$; $K = 8.27$; $H_2O = 3.99$.

$C_6H_3O_3I_2SK, H_2O$ requires $C = 15.45$; $H = 1.12$; $K = 8.36$;
 $H_2O = 3.86$ per cent.

The *silver* salt is only sparingly soluble in water, crystallising in fine, woolly needles; the *copper* salt crystallises in small, pale blue needles; the *cobalt* in small, pink, glistening plates; the *nickel* in pale green, sparkling plates; the *manganese* and the *cerium* in small, white plates.

2: 5-Di-iodobenzenesulphonyl Chloride.—The chloride, prepared from the potassium salt, and also from the anhydrous acid, separates from ether in white needles, melting at 131—132°:

Found, $C = 17.00$; $H = 0.81$.

$C_6H_3O_2ClI_2S$ requires $C = 16.80$; $H = 0.70$ per cent.

A mixture of the sulphonyl chloride with the anhydride is obtained when excess of phosphorus pentachloride or a mixture of phosphorus pentachloride and phosphoryl chloride is used in its preparation;

the anhydride being insoluble in ether, the separation of the two is easily effected. The *anhydride* is a white, amorphous powder, melting at 235—245°; it is stable in air, insoluble in cold water, partly soluble in hot water, giving an acid solution, and is hydrolysed on boiling vigorously with alkali; on boiling with absolute alcohol, an ester, melting at 113°, is obtained.

2: 5-*Di-iodobenzenesulphonamide*.—This is prepared by boiling the chloride with ammonia; it is practically insoluble in hot or cold water, and soluble in alcohol, but it does not crystallise from this solvent, so that, in order to purify it for analysis, it was boiled repeatedly with water and dried, first on a porous plate, and then at 100°:

Found, C=17·71; H=1·14.

$C_6H_5O_2NI_2S$ requires C=17·60; H=1·22 per cent.

Ethyl 2: 5-Di-iodobenzenesulphonate.—This was prepared by the action of alcohol on the chloride in presence of sodium hydroxide, or by treating an ethereal solution of the chloride with sodium ethoxide in alcoholic solution; after the addition of water, the ester was extracted by ether, which, on evaporation, yielded colourless needles, melting at 112·5°.

2: 5-*Di-iodobenzenesulphonyl Chloride Dichloride*.—On passing a rapid stream of dry chlorine into a solution of the chloride in chloroform, a yellow colour is first developed, and after an interval yellow crystals begin to separate. These form stout, glistening, yellow needles, melting at 128—129°; they liberate iodine from potassium iodide. On comparing the behaviour of the dichlorides of *o*-, *m*-, and *p*-iodobenzenesulphonyl chloride, it is obvious that the ortho- is much less readily formed than the meta- and para-compounds; in the present instance, therefore, it may be assumed that it is the iodine in the meta-position relatively to the sulphonyl group that becomes tervalent.

0·3872 Gram liberated iodine equivalent to 15·3 c.c. of 0·0997*N*-sodium thiosulphate:

Found, Active chlorine=13·70.

$C_6H_3O_2Cl_3I_2$ requires Active chlorine=14·21 per cent.

3: 5-*Di-iodobenzenesulphonic Acid*.

In order to obtain evidence as to the position occupied by the second iodine atom in di-iodoaniline-*p*-sulphonic acid, it was necessary to remove the amino-group, and to investigate the nature of the di-iodobenzenesulphonic acid so produced. This acid was found to differ from the two which have already been described, and to be 3: 5-di-iodobenzenesulphonic acid.

Both the methods generally used in removing the amino-group, namely, that of boiling the diazo-compound with alcohol, and that of oxidising the hydrazine derivative, have been applied satisfactorily.

Method I.—The amino-acid was diazotised in presence of very slight excess of dilute sulphuric acid, and the diazo-compound, after being collected and washed with alcohol, boiled with a large quantity of methylated spirit under the ordinary pressure; vigorous evolution of nitrogen occurred, and during the course of two or three hours the diazo-compound passed completely into solution, with the production of a deep red colour. After removing the excess of alcohol, sodium chloride was added, and the crude product was boiled with animal charcoal and recrystallised; a good yield of *sodium di-iodobenzenesulphonate* was obtained. It gave an acid melting at 146°, and a chloride melting in the crude state at 87—88°.

Method II.—The diazo-compound of di-iodoaniline-*p*-sulphonic acid is readily reduced by stannous chloride, a yield of the hydrazine compound amounting to 76 per cent. of the amino-acid being obtained.

The crude amino-acid (40 grams) suspended in a very slight excess of hydrochloric acid was diazotised by the requisite amount of sodium nitrite (6.9 grams). In experiments with small quantities of material, it was found more convenient to add slowly to the cooled acid the mixture of nitrite with the sodium salt of the substance to be diazotised, but when larger quantities were employed, it was found impossible sufficiently to dilute the solution of the sodium salt, so as to prevent the latter from crystallising out, without producing a rather unmanageable bulk of liquid. The warm solution of the sodium salt was therefore poured at once into hydrochloric acid, the amino-acid being precipitated in a fine state of division. After diazotisation, the solution of the diazo-salt was poured slowly into a cooled solution of stannous chloride in concentrated hydrochloric acid, when a thick, white precipitate at once separated, which, after several hours, was collected, well washed with cold water, and dried. Examination showed it to consist of an iodohydrazinobenzenesulphonic acid, probably containing water of crystallisation. It is practically insoluble in cold water, but crystallises from much hot water in small, white needles, which, on being exposed to air during several hours, acquire a slight pink tinge; it is insoluble in alcohol, reduces Fehling's solution on warming, reduces an ammoniacal solution of silver nitrate, and is decomposed by copper sulphate, nitrogen being evolved even in the cold, and violently on heating.

Four agents, namely, copper sulphate, ferric chloride, potassium

chromate, and potassium permanganate, have been used to oxidise the hydrazine, but only potassium permanganate is quite satisfactory. Copper sulphate causes removal of the iodine, ferric chloride gives rise to a substance which still contains nitrogen, but which has not been further investigated, and potassium chromate causes removal of part of the iodine with formation of a mixture of monoiodo- and di-iodo-benzenesulphonic acids.

Potassium Chromate as Oxidising Agent.—The recent work of Chattaway on the oxidation of aromatic hydrazines (Trans., 1908, 93, 270) seems to show that the best agents to employ for displacing the hydrazino-group by hydrogen are potassium chromate and potassium permanganate in alkaline solution; both of these have been employed successfully. In the case of the former, the following experiment was carried out.

Fifty grams of potassium chromate and 5.7 grams of potassium hydroxide were dissolved in water, and the solution was heated almost to the boiling point; 10 grams of the hydrazino-derivative were then gradually added to the hot liquid, and the heating was continued until the action, which was at first very vigorous and was accompanied by much frothing, ceased. After a time, green, hydrated chromic oxide was precipitated, and the clear, yellow filtrate deposited crystals of potassium 3:5-di-iodobenzenesulphonate on cooling. On concentrating the mother liquor, crystals of potassium *m*-iodobenzenesulphonate were obtained. The first crop of crystals gave rise ultimately to a di-iodosulphonic acid, melting at 146°; the second, to an acid which could not be crystallised, and to an amide which crystallised from hot water in colourless needles, melting at 148°; it proved, on analysis, to be *m*-iodobenzenesulphonamide:

Found, C=25.47; H=2.22.

$C_6H_6O_2NIS$ requires C=25.48; H=2.12 per cent.

The melting point of *m*-iodobenzenesulphonamide is given as 152° by Langmuir, but repeated recrystallisations of the amide obtained in this experiment did not raise it above 148°.

Potassium Permanganate as Oxidising Agent.—A dilute solution of 2.4 grams of potassium permanganate and 5 grams of potassium hydroxide was heated to about 60—70°, and 10 grams of the hydrazine were gradually added; the addition was continued until the green colour, which was first developed, disappeared, and hydrated manganese dioxide made its appearance. The mixture was then heated until no other solid than manganese dioxide was present, filtered hot, and the pale yellow filtrate concentrated; impure crystals of potassium 3:5-di-iodobenzenesulphonate (6 grams) were obtained. A second crop from the mother liquor

proved identical with the first. The yield amounted to 70 per cent. of the theoretical. Fractional crystallisation of the product separated it into two distinct sets of crystals, namely, less soluble crystals which have not yet been investigated, and more soluble ones identical with those obtained in method I:

Found, C=16·16; H=0·66.

$C_6H_3O_3I_2SK$ requires C=16·07; H=0·67 per cent.

The same di-iodobenzenesulphonic acid may be obtained from di-iodoaniline-*o*-sulphonic acid by a similar series of changes.

Di-iodoaniline-*o*-sulphonic acid gives rise to a hydrazine closely resembling in appearance that obtained from the para-acid. It is insoluble in cold, and very sparingly soluble in hot, water; it gives the ordinary reactions of a hydrazine. When oxidised by alkaline permanganate, it yields a potassium di-iodobenzenesulphonate, from which an acid, melting at 146°, the melting point of 3:5-di-iodobenzenesulphonic acid, is readily obtained.

3:5-Di-iodobenzenesulphonic acid crystallises from faintly acid solutions in long, radiating crystals, which in the dry state are almost white. It is very soluble in water, moderately soluble in ether, from which it separates in white, soapy crystals, and almost insoluble in mineral acids; it is freed from adhering sulphuric acid by precipitation with concentrated hydrochloric acid, the latter being subsequently removed without difficulty. The crystals from water melt irregularly, beginning at 70°; when dried at 98°, they melt at 138—146°.

Salts of 3:5-Di-iodobenzenesulphonic Acid.—Salts of this acid have been prepared, but only cursorily examined; the *potassium* salt crystallises in large, white plates, the *sodium* in white needles, the *ammonium* and the *barium* in fine, colourless needles.

3:5-Di-iodobenzenesulphonyl Chloride separates from ether in small needles, and from a mixture of ether and light petroleum in clusters of needles, melting at 93°:

Found, C=16·76; H=0·71.

$C_6H_3O_2ClI_2S$ requires C=16·80; H=0·70 per cent.

3:5-Di-iodobenzenesulphonamide is a white powder, insoluble in hot or cold water; it is extremely difficult to purify, and melts irregularly from 205—218°:

Found, C=17·58; H=1·36; I=62·00.

$C_6H_3O_2NI_2S$ requires C=17·60; H=1·22; I=62·10 per cent.

2:4-Di-iodobenzenesulphonic Acid.

Two distinct methods have been used in preparing this acid, the first consisting in preparing 5-nitroaniline-*o*-sulphonic acid and

successively displacing the amino- and nitro-groups by iodine, the second in removing the amino-group from di-iodoaniline-*m*-sulphonic acid by the diazo-reaction. The first method fixes the constitution of the acid, the second affords some evidence as to the constitution of di-iodoaniline-*m*-sulphonic acid; of the two, the former, although involving more operations, is the more convenient, and gives rise to better yields and purer products.

Method I: Preparation of o-Iodo-p-nitrobenzenesulphonic Acid.—The 5-nitroaniline-*o*-sulphonic acid was prepared from *m*-nitroaniline by Post and Hardtung's method (*Ber.*, 1880, **13**, 40; *Annalen*, 1880, **205**, 102), which consists in heating *m*-nitroaniline with fuming sulphuric acid during several hours. As the authors point out, there is much difficulty in so regulating the conditions of temperature and strength of acid that carbonisation shall not occur; in many experiments, when quantities given by the authors (nitroaniline with five times its weight of fuming acid) were gradually heated in an oil-bath, the whole mass decomposed at a temperature far below that given as the temperature of sulphonation. It has been found, however, that if the mixture be kept well shaken, and the oil-bath be gradually heated to 160°, allowed to cool, and again heated to 160° with constant agitation, the heating being continued during two or three hours, sulphonation is complete; a shorter time than two hours leaves some nitroaniline unattacked. The acid mixture is neutralised with barium carbonate, the brown barium salt collected, purified, and decomposed with dilute sulphuric acid; the sulphonic acid crystallises out from the clear filtrate.

21.8 Grams of this nitroaminosulphonic acid were dissolved in water with the addition of a little sodium carbonate, the solution being kept hot and sufficiently dilute to prevent the precipitation of the sodium salt, which tends to separate as a bright yellow precipitate; the clear, hot solution was then poured into excess of dilute sulphuric acid and the mixture well cooled; on the gradual addition of 7 grams of sodium nitrite, the dark yellow colour of the nitro-compound became much paler, and, on complete diazotisation, a very pale yellow diazo-compound separated from the acid mixture. After adding 25 grams of potassium iodide, the mixture was heated on the water-bath until the evolution of nitrogen was at an end; the cooled filtrate, after concentration, deposited crystals. These were collected and recrystallised, separating from water in orange-yellow, shining rhombs, which consisted of potassium *o*-iodo-*p*-nitrobenzenesulphonate. The yield amounted to 30 grams, which is approximately 90 per cent. of the theoretical.

Preparation of m-Iodoaniline-p-sulphonic Acid.—A solution of 15 grams of potassium *o*-iodo-*p*-nitrobenzenesulphonate, with 90 grams of crystallised ferrous sulphate, was heated on the water-bath, and potassium hydroxide (35.5 grams) was slowly added to the hot mixture. After two hours' digestion on the water-bath, reduction was complete; hydrochloric acid then precipitated a white, crystalline mass of the iodoanilinesulphonic acid from the concentrated filtrate.

m-Iodoaniline-p-sulphonic acid crystallises from water in white, feathery needles; it closely resembles, in appearance and properties, the iodoaminosulphonic acids which have been already described. It is much less soluble in water than the idonitro-acid from which it is produced, the addition of mineral acid to a solution of the potassium salt of the latter causing no precipitation of the corresponding acid.

The appearance, therefore, of a white precipitate on the addition of mineral acid may be taken to indicate that reduction has proceeded satisfactorily; separation of the amino-acid from any unchanged nitro-acid is thus easily effected.

Preparation of 2:4-Di-iodobenzenesulphonic Acid.—*m*-Iodoaniline *p*-sulphonic acid yields a very pale yellow diazo-compound; the addition of potassium iodide to a solution of the latter causes evolution of nitrogen and formation of a reddish solution, from which potassium 2:4-di-iodobenzenesulphonate separates on concentration; this salt crystallises in cream-coloured, shining plates. The yield is about 70 per cent. of the theoretical. Addition of barium chloride causes precipitation of the barium salt, and the latter, when decomposed with sulphuric acid, yields, on concentration of the solution, the sulphonic acid in shining needles.

Method II.—The second method of preparing the acid involves the use of di-iodoaniline-*m*-sulphonic acid, which is easily obtained in a pure condition from aniline-*m*-sulphonic acid.

Attempts to remove the amino-group by boiling the diazo-compound with alcohol proved unsuccessful; oxidation of the hydrazine by alkaline chromate yielded, however, satisfactory results. The hydrazine is obtained as a thick, white precipitate, which, on keeping, becomes slightly coloured. It is practically insoluble in hot or cold water and attempts to purify it by recrystallisation from hot water resulted in the production of a slightly coloured solution, from which no crystals could be obtained; the substance was purified, therefore, by boiling it several times with water, after which it was collected and dried. It gives all the reactions of a hydrazine. Attempts to oxidise the hydrazine with copper sulphate resulted in the production of cuprous iodide;

oxidation with alkaline chromate gave, however, the desired result. The same proportions as before were used, and the hydrazine was added gradually to the hot alkaline solution of potassium chromate; violent evolution of nitrogen occurred, and hydrated chromic oxide was gradually precipitated; the cooled, concentrated filtrate deposited crystals of potassium 2:4-di-iodobenzenesulphonate.

2:4-Di-iodobenzenesulphonic acid is very soluble in water. It separates from concentrated solutions in small needles which contain water of crystallisation; this is lost after several hours' exposure in a desiccator, or after a few minutes at 98°. The anhydrous acid melts at 167° to an opaque liquid, which becomes transparent at 172°. The dry acid dissolves readily in ether; the crystals which separate on evaporation of the solvent are very deliquescent, becoming, however, dry and powdery, and melting at 167°, when dried for a few minutes at 98°. The acid is precipitated from its aqueous solution by concentrated hydrochloric acid; use is made of this property in its purification.

Salts of 2:4-Di-iodobenzenesulphonic Acid.—The sodium salt crystallises from water in glistening, white scales, the potassium salt in sparkling, plate-like needles, the ammonium and the barium salts in small, white needles. Solubility determinations have not yet been made, but, owing to the considerable loss entailed in the preparation of the pure barium salt from the potassium salt, there is no doubt that the former is considerably more soluble than the corresponding salts of the isomeric acids.

2:4-Di-iodobenzenesulphonyl Chloride separates from ether in white scales, melting at 77—78°; from a mixture of benzene and light petroleum, it crystallises in rhombic plates:

Found, C=16.90; H=0.98.

$C_6H_3O_2ClI_2S$ requires C=16.80; H=0.70 per cent.

The amide prepared (1) from the potassium salt obtained after removing the amino-group from di-iodoaniline-*m*-sulphonic acid, (2) from the acid obtained directly from 5-nitroaniline-*o*-sulphonic acid, melts at 230°.

3:4:5-Tri-iodobenzenesulphonic Acid.

On passing two molecular proportions of iodine chloride into a dilute solution of aniline-*p*-sulphonic acid, di-iodoaniline-*p*-sulphonic acid, described by Kalle and Co. (*loc. cit.*) as a brown substance rather insoluble in water, is obtained. No difficulty has been experienced in obtaining it free from the monoiodo-derivative; it is an advantage to use a slight excess of iodine chloride, since, as it is impossible to introduce a third atom of iodine into the nucleus, the excess simply ensures complete iodination of the acid. It

crystallises from much hot water; a more convenient method of purification, however, consists in converting the crude substance into its sodium salt, and precipitating the amino-acid from a solution of the latter by the addition of mineral acid. The displacement of the amino-group by iodine, with formation of potassium tri-iodobenzenesulphonate, is readily brought about. The diazo-anhydride of di-iodoaniline-*p*-sulphonic acid is bright yellow, and is decomposed by potassium iodide at 30°. At that temperature, nitrogen begins to be evolved, and a fine, silky precipitate takes the place of the somewhat granular diazo-compound, the precipitate forming a thick scum on the surface of the liquid. A yield of 13 grams from 10 grams of the amino-acid, amounting to 97 per cent. of the theoretical, was obtained.

Potassium 3:4:5-tri-iodobenzenesulphonate is insoluble in cold, and very sparingly soluble in hot, water, from which it crystallises in small, yellowish-white needles; these were dried at 100° for analysis:

Found, C=12.69; H=0.39; I=66.43; K=6.76.

$C_6H_2O_3I_3SK$ requires C=12.54; H=0.34; I=66.38;
K=6.79 per cent.

The barium, lead, and silver salts are all very sparingly soluble in water and in hydrochloric, acetic, and nitric acids respectively. When the barium salt is boiled with excess of concentrated hydrochloric acid, it dissolves to a slight extent, and is at once precipitated if the solution is cooled; it is therefore difficult to detect traces of sulphuric acid or of sulphate in this substance, since the difference in solubility between barium tri-iodobenzenesulphonate and barium sulphate is not very marked. As a whole, sparing solubility may be regarded as characteristic of the salts of this and of the isomeric tri-iodosulphonic acids. The great stability and insolubility of the lead salt was demonstrated by an attempt to prepare the sulphonic acid from it by decomposition with hydrogen sulphide.

The lead salt was suspended in water, and hydrogen sulphide was passed through to saturation; after passing the gas during two or three hours the major portion of the iodo-salt was still unattacked, and it was not until it had been passed into the mixture, which was heated at intervals, for two or three days, that the lead was completely precipitated as lead sulphide, and a clear solution of the sulphonic acid was obtained on filtration. On concentrating the solution, needle-like crystals of the acid, melting at 150—157°, were obtained.

In a second attempt to isolate the sulphonic acid, the calcium salt was heated with the requisite amount of oxalic acid; no change in appearance and practically no decomposition occurred.

A third series of experiments involved the preparation of the barium salt and its decomposition with sulphuric acid, and in this case the acid was obtained without much difficulty. The main difficulty lies in the preparation of the barium salt, the great insolubility of the potassium salt rendering its decomposition by barium chloride a difficult matter when large quantities are being manipulated. The most satisfactory results were obtained when the potassium salt was suspended in much water, excess of barium chloride added, and the mixture boiled during many hours until the yellow scum of potassium salt had entirely disappeared, and until the white precipitate collected after repeated washings by decantation with hot water gave no test for potassium. The barium salt was then boiled with excess of dilute sulphuric acid until the crystalline salt had given place to the heavy barium sulphate; on cooling the concentrated filtrate, a mass of glistening crystals of the sulphonic acid separated.

The acid is extremely soluble in water, moderately so in ether, and insoluble in acids; it is best freed from any adhering sulphuric acid by adding concentrated hydrochloric acid to its aqueous solution, and treating the precipitated acid as described in the case of 3:4-di-iodobenzenesulphonic acid; from acid solutions it crystallises in cream-coloured plates. On account of the difficulty of obtaining good crystals from water, no attempt has yet been made to determine whether or not it contains water of crystallisation, but, judging from analogy to the two isomeric tri-iodobenzenesulphonic acids, and considering the variation in the melting point as the acid is dried under varying conditions, there is little doubt that it does. The melting point of the acid (1) precipitated by mineral acids, (2) separated from ether, (3) crystallised from water and air-dried, or (4) dried at 95° , is 158° ; after being dried at 125° , it melts at 221° . The latter may therefore be regarded as the melting point of the anhydrous acid.

Salts of 3:4:5-Tri-iodobenzenesulphonic Acid.—The *sodium* salt crystallises from water in fine, cream needles, the *potassium* salt in small needles, the *ammonium* salt in long, colourless needles; the *barium*, *lead*, and *silver* salts have all been obtained by precipitation, but have not been prepared in a crystalline condition.

3:4:5-Tri-iodobenzenesulphonyl Chloride separates from ether in small, white needles, and from a mixture of light petroleum and ether in rhombic plates, melting at 145° :

Found, C=13.19; H=0.54.

$C_6H_2O_2Cl_3S$ requires C=12.98; H=0.36 per cent.

The *amide* is a yellowish-white substance, insoluble in hot or cold water; it crystallises from methylated spirit in fine, transparent needles, melting above 250° .

The *anilide* crystallises from alcohol in short, transparent needles, melting at 201° :

Found, C = 23.73; H = 1.42.

$C_{12}H_5O_2NI_3S$ requires C = 23.57; H = 1.30 per cent.

2: 3: 5-Tri-iodobenzenesulphonic Acid.

It has already been stated that when one molecular proportion of iodine chloride is passed into a solution of aniline-*o*-sulphonic acid, *p*-iodoaniline-*o*-sulphonic acid is produced, which, being insoluble in water, separates in purplish-grey crystals as it is formed. Owing to the sparing solubility of this monoiodo-acid great difficulty was to be expected, and has been experienced, in preparing the di-iodo-derivative in a state of purity.

Although the preparation of the tri-iodosulphonic acid does not necessitate the production of a pure amino-acid, the potassium di-iodo- and tri-iodo-sulphonates formed from a mixture of monoiodo- and di-iodo-amino-acids by displacement of the amino-groups by iodine being readily separated by fractional crystallisation, it was thought advisable to determine the conditions favouring the formation of the more highly iodinated product and to obtain it, if possible, in a pure state.

The best method of preparing di-iodoaniline-*o*-sulphonic acid is to pass excess of iodine chloride into a dilute solution of the monoiodo-acid. On adding hydrochloric acid to the solution of the monoiodo-acid, the latter began to separate out, but, as iodine chloride was passed through, this suspended acid gradually dissolved; a clear, reddish-brown solution was obtained, which yielded, after concentration, a large amount of the desired di-iodo-acid. This method of preparation involved the use of small quantities of material; to prepare the acid on the large scale, it was found advisable to precipitate the monoiodo-acid in a fine state of division, and then to pass iodine chloride through the suspended material, with frequent agitation, until the grey crystals of the monoiodo-gave place to the heavy, violet needles of the di-iodo-acid; these were collected and dried.

The acid yields a bright yellow diazo-compound, which is decomposed by potassium iodide, with the production of flaky crystals of potassium 2: 3: 5-tri-iodobenzenesulphonate. The yield of potassium salt is theoretical.

The barium, lead and silver salts, obtained by precipitation from the potassium salt, are all very sparingly soluble in water; the same difficulty, therefore, attends the preparation of the pure barium salt and of the acid from the barium salt as in the case of 3: 4: 5-tri-iodobenzenesulphonic acid. The potassium salt must be boiled for a long time with excess of barium chloride before

complete decomposition occurs; the barium salt must then be boiled with excess of sulphuric acid until, on evaporating the clear filtrate, an acid is obtained which leaves no residue when heated on platinum foil.

From a mineral acid solution, the sulphonic acid separates in shining crystals, which dissolve readily in water, less readily in ether, and are almost insoluble in mineral acids; from water alone, they crystallise in colourless plates, which become rather coloured when exposed to air. The melting point of the air-dried material was found to vary somewhat irregularly; it was usually 166—170°, sometimes 183°, and once above 200°. One can only account for these variations by assuming that the acid, which contains water of crystallisation, loses this gradually; consideration of the melting points obtained when the acid is dried at different temperatures confirms this assumption. When recrystallised from water and examined at once, the melting point is 166—170°; when dried at 95°, it is 183°; and when dried at 135°, it is 210—215°. Analyses showed that it probably crystallises with three molecules of water; 166—170° is therefore the melting point of the hydrated, and 210—215° that of the anhydrous material:

1·2191 lost 0·1137 H₂O when heated during several hours at 135°. H₂O=9·32.

C₆H₃O₃I₃S·3H₂O requires H₂O=9·15 per cent.

Salts of 2:3:5-Tri-iodobenzenesulphonic Acid.—The sodium, potassium, and ammonium salts obtained by neutralisation, and the lead, barium, silver, copper, manganese, nickel, and cobalt salts obtained by precipitation have all been prepared. The sodium salt crystallises in transparent needles, the ammonium salt in white needles, and the potassium salt in shining plates; of the others, the barium and silver salts are extremely difficult to crystallise, the lead salt separates in small, woolly needles, the copper salt in pale blue plates, the nickel salt in small, green needles, the cobalt salt in pink plates, and the manganese salt in fine, white, feathery needles.

2:3:5-Tri-iodobenzenesulphonyl Chloride separates from ether in small, white needles, and from a mixture of benzene and light petroleum in long, transparent needles, melting at 122—123°:

Found, C=13·01; H=0·42.

C₆H₂O₂ClI₃S requires C=12·98; H=0·36 per cent.

The *amide* is a white powder, insoluble in hot or cold water, and very sparingly soluble in alcohol; it does not melt below 280°.

Ethyl 2:3:5-tri-iodobenzenesulphonate was prepared from the sulphonyl chloride by treating it with absolute alcohol in the presence of excess of sodium hydroxide. It separates from ether in clusters of needles, melting at 110°:

Found, C = 16.91; H = 1.35.

$C_8H_7O_2I_3S$ requires C = 17.02; H = 1.24 per cent.

2:4:5-Tri-iodobenzenesulphonic Acid.

In Kalle and Co.'s patent (*loc. cit.*), it was stated that the passage of two molecular proportions of iodine chloride into a solution of aniline-*m*-sulphonic acid containing a little hydrochloric acid resulted in the formation of di-iodoaniline-*m*-sulphonic acid, which separated out as it was formed. No mention was made of any monoiodoaniline-*m*-sulphonic acid, and the conclusion was therefore drawn that such a substance could not be isolated under these conditions. It was not, therefore, until quite recently, after the di-iodo-derivative had been converted into the tri-iodosulphonic acid and subjected to investigation, that any attempt was made to discover whether the mono-derivative could be obtained, and, if so, what conditions favoured its production. It will be seen from the theoretical part of this paper that a knowledge of the constitution of monoiodoaniline-*m*-sulphonic acid is useful in fixing the constitution of the di-iodo-derivative, and, consequently, of the tri-iodosulphonic acid formed from it; it seems advisable, therefore, to give experimental details of its preparation here when substances prepared from aniline-*m*-sulphonic acid are being discussed.

In one experiment, slightly less than one molecular proportion of iodine chloride was passed into a very dilute solution of aniline-*m*-sulphonic acid (8.6 grams in 2 litres of water), and the dark brown liquid was kept for several hours; a violet colour was gradually developed, and, on cooling the concentrated solution, yellowish-brown crystals separated; these, after being diazotised and treated with potassium iodide, yielded crystals of potassium 3:4-di-iodobenzenesulphonate in an impure condition. The acid obtained from this salt melted irregularly at 115—117° (3:4-di-iodobenzene-sulphonic acid melts at 122—125°), the low melting point indicating that some amino-acid had probably escaped iodination in the first instance, and that the final product was therefore a mixture of the di-iodo- with some monoiodo-sulphonic acid. The conversion of a fresh quantity of the potassium salt, dried at 100°, into the chloride, afforded convincing evidence of its constitution; the chloride crystallised from a mixture of light petroleum and benzene in transparent needles, which became white and opaque when left in a desiccator over sulphuric acid, and melted sharply at 82°, the melting point of 3:4-di-iodobenzenesulphonyl chloride.

There is no doubt, therefore, that when iodine chloride acts on aniline-*m*-sulphonic acid, a monoiodo-derivative is formed, in which the iodine atom occupies the position ortho- and para- to the amino- and sulphonic groups respectively; the second iodine atom, as has

already been shown, enters the para-position with respect to the amino-group. Di-iodoaniline-*m*-sulphonic acid yields a yellow diazo-compound, which is decomposed by potassium iodide, with formation of 2:4:5-tri-iodobenzenesulphonic acid, which separates from the hot solution in shining crystals of the potassium salt. The preparation of the barium salt and of the acid from the barium salt are matters of little difficulty, the acid separating on evaporation of its aqueous solution in shining plates. It dissolves very readily in water, more sparingly in ether, and is almost insoluble in mineral acids; the crystals from water melt sharply at 182°; when dried at 100°, or at 125°, they melt at 230°. Analysis showed that the acid melting at 182° contains three molecules of water of crystallisation:

Found, C = 12·32; H = 1·69; H₂O = 9·14.

C₆H₃O₃I₃S·3H₂O requires C = 12·20; H = 1·50; H₂O = 9·15 per cent.

Salts of 2:4:5-Tri-iodobenzenesulphonic Acid.—The *sodium* and *potassium* salts crystallise in long, white needles; the *ammonium* salt in small, white nodules; the *potassium* salt crystallises with one molecule of water:

Found. C = 12·34; H = 0·66; H₂O = 3·34.

C₆H₂O₃I₃SK·H₂O requires C = 12·16; H = 0·67; H₂O = 3·04 per cent.

2:4:5-Tri-iodobenzenesulphonyl Chloride crystallises from ether in small needles, and from a mixture of light petroleum and ether in small, sparkling crystals, melting at 135°:

Found, C = 12·96; H = 0·40.

C₆H₂O₂ClI₃S requires C = 12·98; H = 0·36 per cent.

The *amide* is a yellowish-white powder, insoluble in water, but soluble in methylated spirit; it does not melt below 260°:

Found, C = 13·45; H = 0·70; I = 71·21; N = 2·37.

C₆H₄O₂I₃NS requires C = 13·45; H = 0·74; I = 71·21;
N = 2·61 per cent.

The *anilide* crystallises from alcohol in small, needle-shaped crystals, melting at 194—196°:

Found, C = 23·67; H = 1·49.

C₁₂H₈O₂I₃NS requires C = 23·27; H = 1·31 per cent.

My thanks are due to Professor H. E. Armstrong, through whose suggestion the work arose; to Miss E. E. Field, for kind help and encouragement during its progress; and to Miss M. Tutin, for valuable help in the preparation of material and in the analysis of salts.

CLXXXVII.—*The Influence of Gaseous Oxides of Nitrogen on the Rate of Interaction of Chlorine and Hydrogen.*

By DAVID LEONARD CHAPMAN and PATRICK SANSFIELD MACMAHON.

HITHERTO it has been shown that both oxygen (Bunsen and Roscoe, *Phil. Trans.*, 1857, **147**, 390) and nitrogen chloride (Burgess and Chapman, *Trans.*, 1906, **89**, 1399) retard the union of hydrogen and chlorine in light, and that, although the inhibitive influence of the former is considerable, that of the latter is incomparably greater. On the other hand, the observed retardation of the same reaction by nitrogen and carbon dioxide was so small that we have been forced to conclude that these gases function as diluents only. The fact that the property of inhibiting the union of hydrogen and chlorine is strictly limited to a few substances, and is not possessed in varying degrees by gases in common, suggests that it is the result of some chemical relation, definable in general terms, between the gas exhibiting the property and one or more of the constituents of the interacting system. It is possible that the inhibitor must be capable of reacting with one or more of the other gases present. Such a condition is obviously satisfied by oxygen and nitrogen chloride.

As this conjecture is supported by facts recently disclosed in the study of the effect of the gaseous oxides of nitrogen on the rate of union of chlorine and hydrogen, it is advanced tentatively as a hypothesis which will at least serve to indicate the line of investigation that we intend to pursue.

In the presence of water, nitric oxide and chlorine interact, and a brown gas, probably nitrogen peroxide, results. A considerable period of time elapses before the last trace of this gas is absorbed by the chlorine water in the vessel containing it. If a comparatively small volume of nitric oxide is introduced into a mixture of chlorine and hydrogen, the resulting brown gas inhibits the interaction of the chlorine and hydrogen in the light. When, on standing for several hours, the nitrogen peroxide has dissolved, the electrolytic gas almost recovers its former sensitiveness. In its power to retard the interaction of chlorine and hydrogen, nitrogen peroxide appears to lie between nitrogen chloride and oxygen. Like oxygen, nitrogen peroxide will, under the conditions necessary for the interaction of chlorine and hydrogen, act on hydrogen chloride, so that it belongs to that class of substances to which the property of inhibition is supposed to be limited.

Nitrogen monoxide, although an oxidising agent, acts merely as a diluent. Nitrous oxide is, however, an extremely stable and inert substance at the ordinary temperature. It is probable that it will only part with its oxygen at elevated temperatures.

The three known inhibitors, therefore, contain either loosely combined atoms of oxygen or loosely combined atoms of chlorine. They are all three capable of oxidising hydrogen chloride, and if it is assumed that a comparatively large amount of energy is dissipated in the process of oxidation, an intelligible explanation is afforded of the means by which the inhibitor is enabled to discharge the efficient energy of the chlorine.

The facts published in our last paper on the retarding effect of oxygen (this vol., 959) are in complete harmony with the theory. The communication in question contained experimental evidence which pointed to the conclusion that a very small (perhaps an infinitely small) amount of light energy was sufficient to cause the union of considerable amounts of chlorine and hydrogen in a mixture of the gases containing no oxygen or other inhibitor. On the other hand, to oxidise with gaseous oxygen an equivalent quantity of hydrogen chloride in the presence of chlorine, must necessitate the expenditure of a considerable amount of efficient energy. It is, therefore, not surprising that oxygen, although an inhibitor, is not removed from a mixture of hydrogen and chlorine at a measurable rate in the presence of light.

EXPERIMENTAL.

The apparatus was the same as that employed to measure the retarding effect of oxygen. The electrolytic gas was so free from inhibitive impurities removable by the action of light that no induction period could be observed when the actinometer filled with the mixture was exposed to light. The nitric oxide was prepared by the action of dilute nitric acid on a saturated solution of ferrous sulphate, and was collected in a large gasholder filled with water. After standing in the presence of the water for several hours, some of the gas was allowed to pass into a smaller gasholder filled with a boiled solution of sodium arsenite, in the presence of which reagent it was allowed to remain for several days in order to remove any nitrogen chloride which might be present. As the light emitted from the standard Hefner lamp was inconveniently feeble for these experiments, an electric glow-lamp of 25 c.p., placed at a distance of 2 metres from the insolation vessel, was substituted for it. Under the influence of the light from this lamp, the index of the actinometer moved at the rate of 40 cm. in one minute. A measure

of nitric oxide, equal to 1/300th of the total volume, was admitted. The mixture was then exposed to the light of the glow-lamp for half an hour, during which period there was no detectable movement of the index. If the original mixture had been exposed to the light for the same length of time, about one-third of the electrolytic gas would have been converted into hydrogen chloride. After the illumination of half an hour, the mixture was allowed to stand in the dark for two and a-half hours, and then re-exposed to light; during twenty-five minutes there was no combination. The actinometer was then left for thirteen hours in the dark. On exposure to light there was instantaneous formation of hydrogen chloride. The movement of the index was at first slow, but it gradually increased until the sensitiveness of the mixture was almost as great as that observed before the nitric oxide had been added.

In a second experiment the procedure was slightly varied. Fresh water was introduced into the actinometer, which was subsequently filled with sensitive electrolytic gas. The index liquid moved 34 cm. in one minute when the insolation vessel was exposed to the light of the glow-lamp; but after the mixture had been left for almost twelve hours in darkness, the nitrogen peroxide had almost completely disappeared from the gas. The sensitiveness, which was at first only 3 cm. per minute, increased gradually and rather irregularly to its original value.

In a third experiment it was found that a mixture of the same composition began to combine after five hours' continuous exposure to light. A soluble product of the interaction of moist nitric oxide and chlorine, presumably nitrogen peroxide, is therefore capable of inhibiting the combination of chlorine and hydrogen.

In the experiments with nitrous oxide, some difficulty was presented in the preparation of the gas sufficiently pure for our purpose. Very small quantities of foreign substances in the ammonium nitrate, from which the nitrous oxide is prepared, tend to facilitate side reactions when the salt is decomposed by heating. The ammonium nitrate was therefore crystallised four times from pure water. In the preparation of the nitrous oxide, great care should be taken to prevent rapid decomposition of the salt. In spite of the precautions taken to ensure purity, we have not succeeded in preparing a sample of the gas quite free from nitric oxide.

In the experiments performed to test the influence of the nitrous oxide on the rate of interaction of chlorine and hydrogen, the source of light was a Hefner lamp, placed at a distance of 60 cm. from the insolation vessel of the actinometer. The details of an experiment are recorded below.

The sensitiveness of the electrolytic gas was 4.40 cm. per minute. After adding to the electrolytic gas 1/300th of its volume of nitrous oxide, it was found that hydrogen chloride was still formed in the light, the rate of its formation corresponding to a movement of the index of 0.36 cm. per minute. On standing for 12.5 hours in darkness, the sensitiveness was 2.30 cm. per minute, but it rose gradually to 4.00 cm. per minute. That the observed retardation immediately after the addition of the nitrous oxide was not caused by the nitrous oxide itself, but by a small amount of nitric oxide, is evident from the circumstance that the effect almost entirely disappeared after the insolation vessel had been allowed to remain in darkness for half a day. Another experiment, in which a volume of nitrous oxide equal to as much as 1/20th of the internal capacity of the insolation vessel was added, furnished similar results.

Conclusions.

1. A gaseous product of the interaction of moist chlorine and nitric oxide (presumably nitrogen peroxide) inhibits the interaction of chlorine and hydrogen.

2. The inhibitive gas is after several hours almost completely absorbed by the chlorine water.

3. Nitrous oxide is a mere diluent. The rate of interaction of chlorine and hydrogen is not appreciably affected by the presence of a comparatively large volume of the gas.

4. It is considered as probable that the action of the inhibitor is such that the efficient energy of the chlorine derived directly from the light is dissipated by its bringing about a chemical change in which the inhibitor takes part.

THE SIR LEOLINE JENKINS LABORATORIES,
JESUS COLLEGE,
OXFORD.

CLXXXVIII.—*Further Syntheses of p-Hydroxyphenylethylamine.*

By GEORGE BARGER and GEORGE STANLEY WALPOLE.

ONE of us described recently (Trans., 1909, 95, 1123) the isolation of a new physiologically active principle of ergot, its identification as *p*-hydroxyphenylethylamine, and its synthesis by the reduction of *p*-hydroxyphenylacetonitrile. On account of the therapeutical

interest of the substance, other syntheses were attempted, and two of these form the subject of the present paper.

In the first place, the introduction of a phenolic hydroxyl group into phenylethylamine was attempted. By nitrating benzoylphenylethylamine, a *p*-nitro-derivative was readily obtained, and this yielded by successive reduction and diazotisation the *N*-benzoyl derivative of the desired substance, which was readily converted into *p*-hydroxyphenylethylamine itself by heating with acids. Instead of benzylation, we also used acetylation as a means of protecting the amino-group, but in this case the *p*-nitro-derivative is not so readily separated from its isomerides. Phenylethylamine can also be nitrated in the form of its benzylidene derivative when dissolved in concentrated sulphuric acid, but the mixture of nitro-compounds, which results on dilution with water, cannot be separated except by acetylation or benzylation.

The second synthesis to be described starts from anisaldehyde, which was converted into *p*-methoxyphenylpropionic acid. This acid, first prepared by W. H. Perkin, sen. (Trans., 1877, **31**, 411), is more readily obtained by the method given by Perkin, jun., and Robinson for 3:4-dimethoxyphenylpropionic acid (Trans., 1907, **91**, 1071). The amide of this acid, $\text{MeO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$, yielded by Hofmann's reaction *p*-methoxyphenylethylamine, $\text{MeO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$, from which the methyl group was finally removed by heating with hydrobromic acid.

EXPERIMENTAL.

I.—*Synthesis of p-Hydroxyphenylethylamine from Phenylethylamine.*

Benzoyl-p-nitrophenylethylamine, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NHBz}$, was prepared by slowly adding benzoylphenylethylamine (8 grams) to fuming nitric acid (40 grams), the temperature being kept below 5°. After pouring on snow, the product solidified. On crystallisation from alcohol, 3·4 grams of the para-compound separated in long needles; the mother liquor contains isomeric nitro-compounds, which are much more soluble.

Benzoyl-p-nitrophenylethylamine was obtained pure by a second crystallisation from alcohol, and then melted at 162°. It is moderately soluble in boiling alcohol, but only sparingly so in cold alcohol:

0·2573 gave 22·2 c.c. N_2 (moist) at 11° and 748 mm. $\text{N}=10\cdot0$.

$\text{C}_{15}\text{H}_{14}\text{O}_3\text{N}_2$ requires $\text{N}=10\cdot4$ per cent.

Benzoyl-p-aminophenylethylamine, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NHBz}$.

Benzoyl-*p*-nitrophenylethylamine (13.5 grams) is suspended in 100 c.c. of alcohol, tin foil (11 grams) is added, and then gradually 50 c.c. of concentrated hydrochloric acid. The temperature is at first kept below 50°; finally the reaction is completed on the water-bath. When all the tin has dissolved, the solution is filtered, and the alcohol is removed by steam distillation. On cooling, the hydrochloride of the amino-compound separates. The free base was obtained by rendering the solution alkaline and extracting with ether. It forms crystals, melting at 134°:

0.3183 gave 31.4 c.c. N_2 (moist) at 17° and 759 mm. $\text{N} = 11.5$.

$\text{C}_{15}\text{H}_{16}\text{ON}_2$ requires $\text{N} = 11.6$ per cent.

The *hydrochloride* melts and decomposes above 280°, and is very sparingly soluble in water:

0.2677 gave 0.1376 AgCl. $\text{Cl} = 12.7$.

$\text{C}_{15}\text{H}_{16}\text{ON}_2 \cdot \text{HCl}$ requires $\text{Cl} = 12.7$ per cent.

Benzoyl-p-hydroxyphenylethylamine, $\text{HO} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NHBz}$.

To a boiling solution of the amino-compound in dilute sulphuric acid, a solution of sodium nitrite was slowly added in equivalent proportion. The hydroxy-compound formed is almost insoluble in water, and separated out; it was collected and crystallised from alcohol, when it formed hexagonal plates, melting at 162°:

0.1300 gave 6.5 c.c. N_2 (moist) at 15° and 750 mm. $\text{N} = 5.8$.

$\text{C}_{15}\text{H}_{14}\text{O}_2\text{N}$ requires $\text{N} = 5.8$ per cent.

On heating with 20 per cent. hydrochloric acid to 140°, this substance is hydrolysed, yielding *p*-hydroxyphenylethylamine; on benzylation by the Schotten-Baumann method, the dibenzoyl derivative, melting at 170°, is formed.

Acetyl-p-nitrophenylethylamine, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NHAc}$, is prepared by adding acetylphenylethylamine to nitric acid in the same way as was described for the benzoyl compound. After pouring on snow, the acetyl derivative, unlike the benzoyl derivative, remained liquid. The solution was therefore extracted with ether, and the ethereal solution was washed with sodium carbonate to free it from nitric acid, dried, and evaporated. Very little methyl alcohol was added to the syrupy residue; on keeping in a vacuum desiccator, crystals were slowly deposited, which were pressed on a porous tile, and recrystallised from methyl alcohol; they then melted at 142°:

0.1326 gave 0.2836 CO_2 and 0.0712 H_2O . C=58.2; H=5.9.

0.0869 ,, 10.2 c.c. N_2 (moist) at 19° and 762 mm. N=13.5.

$\text{C}_{10}\text{H}_{12}\text{O}_3\text{N}_2$ requires C=57.8; H=5.8; N=13.5 per cent.

The nitro-compound thus obtained was reduced, the crude amino-compound diazotised, and the resulting solution was concentrated until it contained about 30 per cent. of sulphuric acid, and heated to 140° . *p*-Hydroxyphenylethylamine was then extracted by amyl alcohol and isolated as the dibenzoyl derivative (m. p. $169\text{--}170^\circ$), but none of the intermediate compounds were characterised.

p-Nitrophenylethylamine, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$.

This substance is readily obtained, mixed with its isomerides, when benzylidenephénylethylamine, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{N}:\text{CHPh}$ (melting at about 70° ; prepared by warming the components), is nitrated in sulphuric acid solution by the addition of the calculated quantity of potassium nitrate. On diluting with water and removing, by steam distillation, the benzaldehyde formed, a yellow oil remains, which, on acetylation and benzoilation, yields the *p*-nitro-derivatives (melting respectively at 142° and 162°), which have been described above. The benzoyl derivative was hydrolysed by heating with ten times its weight of concentrated hydrochloric acid to 170° for four hours. *p*-Nitrophenylethylamine was thus obtained as a yellow syrup, which could not be crystallised, and was readily soluble in most organic solvents. It absorbed carbon dioxide from the air, forming a crystalline carbonate. The *hydrochloride* forms leaflets, melting at 214° , and was analysed:

0.2141 gave 0.1522 AgCl . Cl=17.6.

$\text{C}_8\text{H}_{10}\text{O}_2\text{N}_2\cdot\text{HCl}$ requires Cl=17.5 per cent.

II.—*Synthesis of p-Hydroxyphenylethylamine from Anisaldehyde.*

The *p*-methoxyphenylpropionic acid required was prepared according to the same method as that employed by Perkin and Robinson (*Trans.*, 1907, **91**, 1079) for the preparation of 3:4-dimethoxyphenylpropionic acid.

Anisaldehyde (100 grams) was condensed with ethyl acetate (245 grams) by means of finely-divided sodium (24.5 grams). After one hour, 102 grams of potassium hydroxide, dissolved in methyl alcohol, were added; after removal of the alcohol by distillation, the solution was treated with 3000 grams of $2\frac{1}{2}$ per cent. sodium amalgam. The resulting methoxyphenylpropionic acid was crystallised from water; yield 46 grams, melting point 104° .

p-Methoxyphenylpropionamide, $\text{MeO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$.

The acid obtained above (46 grams) was heated on a water-bath with one molecular proportion of phosphorus pentachloride in chloroform solution until no more hydrogen chloride was evolved. On fractionally distilling the mixture, 30 grams of *p*-methoxyphenylpropionyl chloride, boiling at 161—165°/15 mm., were collected. Gaseous ammonia was passed into the ethereal solution of the chloride, and gave a quantitative yield of the *amide*, which crystallised from alcohol in prisms, melting at 124°:

0·1009 gave 7·2 c.c. N_2 (moist) at 24° and 758 mm. $\text{N}=8\cdot0$.

$\text{C}_{10}\text{H}_{13}\text{O}_2\text{N}$ requires $\text{N}=7\cdot8$ per cent.

p-Methoxyphenylethylamine, $\text{MeO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$.

The amide (27 grams) was heated with 7·9 c.c. of bromine dissolved in 150 c.c. of water containing 36·5 grams of sodium hydroxide, the temperature not exceeding 55°. On extraction of the base with ether, drying, and fractionally distilling, 8 grams of *p*-methoxyphenylethylamine, boiling at 138—140°/20 mm., were obtained. The base forms a colourless liquid, very sparingly soluble in water. On passing hydrogen chloride into the ethereal solution of the base, a crystalline *hydrochloride*, melting at 206°, was obtained:

0·0946 gave 0·0717 AgCl. $\text{Cl}=18\cdot8$.

$\text{C}_9\text{H}_{13}\text{ON}\cdot\text{HCl}$ requires $\text{Cl}=18\cdot8$ per cent.

0·5 Gram of the above hydrochloride was heated for four hours to 160° with 5 c.c. of hydrobromic acid (D 1·4). On cooling, a salt crystallised out, but could not be readily freed from the mother liquor; the excess of hydrobromic acid was therefore removed under diminished pressure, and the remaining solid boiled in alcoholic solution with charcoal. On adding ether to the filtrate, a salt separated which gave Millon's reaction; after benzylation, the dibenzoyl derivative of *p*-hydroxyphenylethylamine, melting at 169—170°, was isolated.

THE WELLCOME PHYSIOLOGICAL RESEARCH LABORATORIES,
HERNE HILL, LONDON, S.E.

CLXXXIX.—*The Preparation of Disulphides. Part VII.
The Nitrobenzyl Mercaptans and Disulphides.*

By THOMAS SLATER PRICE and DOUGLAS FRANK TWISS.

IN an earlier paper (Trans., 1908, **93**, 1402), the authors have described the preparation of the three nitrobenzyl disulphides (ortho, meta, and para) by the action of sodium carbonate on the solution of the corresponding alkyl thiosulphate compound. However, although the properties of the *o*- and *m*-disulphides agreed well with those described by previous observers (Cassirer, *Ber.*, 1892, **25**, 3029; Gabriel and Posner, *Ber.*, 1895, **28**, 1025; Gabriel and Stelzner, *Ber.*, 1896, **29**, 161; Lutter, *Ber.*, 1897, **30**, 1069; Blanksma, *Rec. trav. chim.*, 1901, **20**, 137), the *p*-nitrobenzyl disulphide obtained was entirely different from the substance which Strakosch describes as this compound (*Ber.*, 1872, **5**, 692).

The method of preparation described by Strakosch is to mix *p*-nitrobenzyl chloride with ammonium sulphide in alcoholic solution, when, according to his statement, the mercaptan first separates, and this, on further treatment with ammonium sulphide, gives the disulphide. This statement cannot be correct, for the following reasons. (*a*) The melting point of the mercaptan (140°) is given as being higher than that of the disulphide (89°). (*b*) O. Fischer (*Ber.*, 1895, **28**, 1337) has shown that the action of alcoholic ammonium sulphide on *p*-nitrobenzyl chloride yields much *p*-nitrobenzyl monosulphide (m. p. 159°), and although he suggests that Strakosch's mercaptan is really this compound, he does not appear to have further studied the matter. (*c*) Otto and Rössing (*Ber.*, 1886, **19**, 3129) have shown that the action of potassium sulphide on an organic disulphide in alcoholic solution gives the mercaptan by reduction. (*d*) In a recent paper (Schaeffer and Murúa, *Ber.*, 1907, **40**, 2007), *p*-nitrobenzyl mercaptan is mentioned as having the melting point 51°.*

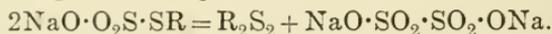
A repetition of Strakosch's experiment showed us that the product of the reaction is really a mixture of the sulphide, disulphide, and mercaptan of *p*-nitrobenzyl, and we have assured ourselves of the true character of the *p*-nitrobenzyl disulphide (m. p. 126·5°) obtained by us previously, in the following manner. Under the action of mineral acids, the sodium alkyl thiosulphates yield the corresponding mercaptans (Bunte, *Ber.*, 1874, **7**, 646; Purgotti,

* The details regarding this substance are given in an Inaugural Dissertation by Waters (Munich, 1905), a copy of which we have not been able to examine.

Gazzetta, 1890, **20**, 25); by this reaction, we have obtained the ortho-, meta-, and para-mercaptans from the three sodium nitrobenzyl thiosulphates. From these mercaptans the corresponding disulphides were prepared by oxidation with iodine, and found to be identical with the compounds we had previously obtained by the action of alkali on the three sodium nitrobenzyl thiosulphates. The only one which was doubtful, in the light of Strakosch's results, was the *p*-disulphide, but any doubt is now removed.

The mercaptans are formed from the alkyl thiosulphate compounds by hydrolysis with acids (Bunte, *loc. cit.*) according to the equation: $\text{RS}_2\text{O}_3\text{Na} + \text{H}_2\text{O} = \text{RSH} + \text{NaHSO}_4$.

This reaction was used by Bunte in support of the formula $\text{NaS}\cdot\text{SO}_2\cdot\text{ONa}$, which is usually assigned to sodium thiosulphate. Gutmann (*Ber.*, 1909, **42**, 228) has recently shown, however, that in the course of the reaction disulphide and sulphur dioxide are produced at the same time as the mercaptan and sulphate. He considers that these results disprove Bunte's interpretation of the reaction, and he explains them by the intermediate formation of the hypothetical compound thioethyl hydroperoxide, $\text{C}_2\text{H}_5\cdot\text{S}\cdot\text{OH}$, which he has also assumed to be formed in other reactions (*Ber.*, 1908, **41**, 1650). At the same time, he throws doubt on the constitutional formulæ usually assigned to sodium thiosulphate and to sodium sulphite. We have previously shown (*Trans.*, 1908, **93**, 1395; *Ber.*, 1908, **41**, 4375) that the usually accepted formulæ give a satisfactory explanation of all Gutmann's results, and that there is no valid evidence for the existence of the thioethyl hydroperoxide; we cannot see that Gutmann's recent results afford any fresh evidence in the matter. That he has found disulphide and sulphur dioxide to be formed in the hydrolysis of sodium and potassium ethyl thiosulphates is readily explained by the thermal decomposition these compounds undergo (compare Bunte and Purgotti, *loc. cit.*). If an aqueous solution of sodium ethyl thiosulphate, or even of sodium benzyl thiosulphate, which is much more stable, is heated for some time, disulphide and dithionate are formed according to the equation:



In the presence of acids, the dithionate is decomposed with the evolution of sulphur dioxide. This reaction is subsidiary to the ordinary hydrolytic one, but will account for all Gutmann's results.

EXPERIMENTAL.

The method of preparation and purification of the mercaptans was practically the same in each case. Ten grams of the nitrobenzyl chloride and 15 grams of sodium thiosulphate were heated

together in 30 c.c. of alcohol (95 per cent.) and 30 c.c. of water under reflux for approximately one hour. The clear solution was allowed to cool, after which the sodium nitrobenzyl thiosulphate, which crystallised out, was collected and washed with a little alcohol. The thiosulphate compound, without further purification, was dissolved in water, and the solution filtered if not quite clear.* After the addition of 7 c.c. of concentrated sulphuric acid, the solution was maintained at a temperature just below its boiling point for about eight hours, by which time the mercaptan had separated as an oil. The yield of the crude mercaptan was approximately 80 per cent.; it could be slightly increased by longer heating. In order to remove the disulphide, which contaminated the crude product, the mercaptan was distilled in an atmosphere of carbon dioxide under diminished pressure. The purity was then tested by titration, in alcoholic solution, with *N*/10-iodine (compare Klason and Carlson, *Ber.*, 1906, **39**, 738).

o-Nitrobenzyl mercaptan forms pale yellow crystals, which melt at 29.5° to a yellow liquid which distils at 149.5°/15 mm. Gabriel and Stelzner (*Ber.*, 1896, **29**, 161) give 42—44°; in all probability their product was contaminated by much disulphide. Oxidation with iodine gave the disulphide, melting at 110°:

0.2758 required 16.22 c.c. of *N*/10-iodine for complete oxidation.
M.W. = 170.1.

$C_7H_7O_2NS$ requires M.W. = 169.1.

m-Nitrobenzyl mercaptan is a bright yellow liquid at the ordinary temperature; it distils at 164°/18 mm. It can be obtained in the form of pale yellow crystals, which melt at 14°. Lutter (*Ber.*, 1897, **30**, 1069) gives 11—12°. On exposure to the air, the liquid oxidises very slowly. Oxidation with iodine gave the disulphide, melting at 103°:

0.4684 required 27.50 c.c. of *N*/10-iodine for complete oxidation.
M.W. = 170.3.

$C_7H_7O_2NS$ requires M.W. = 169.1.

p-Nitrobenzyl mercaptan forms yellow needles, which melt at 52.5°. Schaeffer and Murúa (*Ber.*, 1907, **40**, 2007) give 51°. It distils at 164°/15 mm. Recrystallisation was not a satisfactory method of purification, on account of unavoidable oxidation which took place. Oxidation with iodine gave the disulphide, melting at 126.5°:

0.3454 required 20.40 c.c. of *N*/10-iodine for complete oxidation.
M.W. = 169.3.

$C_7H_7O_2NS$ requires M.W. = 169.1.

* Any turbidity was due to the presence of disulphide, which had been formed by the thermal decomposition of the alkyl thiosulphate.

The nitrobenzyl mercaptans have faint characteristic odours, that of the para-compound being the least pleasant. With an alcoholic solution of lead acetate, the ortho- and para-compounds give an orange-red precipitate; the meta- gives a primrose-yellow precipitate under the same conditions.

Action of Ammonium Sulphide on p-Nitrobenzyl Chloride.

Three c.c. of an approximately 30 per cent. ammonia solution were dissolved in 40 c.c. of alcohol (95 per cent.), and the solution was saturated with hydrogen sulphide. A warm alcoholic solution of 5 grams of *p*-nitrobenzyl chloride was added, when almost immediately needle-shaped crystals began to separate, and hydrogen sulphide was evolved. After five hours, the crystals (A) were collected. They were recrystallised from pyridine, and then from alcohol, the melting point after the recrystallisations being 155° and 156—157° respectively:

0.2400 gave 0.1942 BaSO₄. S=11.1.

C₁₄H₁₂O₄N₂S requires S=10.5 per cent.

The melting point and the analysis indicate that this substance was almost pure *p*-nitrobenzyl sulphide. O. Fischer gives the melting point as 159°.

On the addition of hot alcohol to the mother liquor from the recrystallisation of the sulphide from pyridine, cream-coloured crystals were obtained, which melted at 115—130°. The percentage of sulphur in these crystals (14.8 per cent.) indicated a mixture of disulphide and monosulphide. (The monosulphide requires S=10.5, and the disulphide S=19.0 per cent.)

On the addition of water to the mother liquor from which the last-mentioned solid had separated, a precipitate was obtained which melted at 53—55°, and consisted chiefly of *p*-nitrobenzyl mercaptan. After oxidation with iodine in alcoholic solution, and without further purification, the crystals obtained melted at 124.5°; they were obviously the slightly impure para-disulphide.

After the first lot of crystals (A) had been collected, the mixture deposited more solid after a few days. Determinations of the melting point (125°) and of the sulphur content of this solid, after recrystallisation from a mixture of alcohol and pyridine, showed it to consist mainly of *p*-nitrobenzyl disulphide:

0.3587 gave 0.5050 BaSO₄. S=19.3.

C₁₄H₁₂O₄N₂S₂ requires S=19.0 per cent.

On further keeping for a month or so, the mother liquor again deposited more solid, which, after recrystallisation from a mixture

of alcohol and pyridine, melted at 120—122°. Like the previous solid, this appeared to be chiefly *p*-nitrobenzyl disulphide:

0.1602 gave 0.2239 BaSO₄. S=19.2.

C₁₄H₁₂O₄N₂S₂ requires S=19.0 per cent.

The product of the interaction of ammonium sulphide and *p*-nitrobenzyl chloride is therefore evidently a mixture containing the disulphide, monosulphide, and mercaptan.

We desire to express our thanks to the Research Fund Committee of the Chemical Society for a grant which partly defrayed the expenses of the foregoing investigation.

CHEMICAL DEPARTMENT,
MUNICIPAL TECHNICAL SCHOOL,
BIRMINGHAM.

CXC.—*The Benzyl and Nitrobenzyl Selenosulphates and the Benzyl and Nitrobenzyl Diselenides.*

By THOMAS SLATER PRICE and LIONEL MANFRED JONES.

THE chief methods which have hitherto been used for the preparation of organic diselenides are: (a) Oxidation of the seleno-mercaptans; (b) action of potassium diselenide on the potassium alkyl sulphates; (c) treatment of the monoselenide with selenium; (d) action of sodium diselenide on the alkyl halides; (e) action of selenium on the Grignard compounds. In many cases diselenides are formed as by-products in the preparation of the seleno-mercaptans and monoselenides. (For literature see: Jackson, *Annalen*, 1875, **179**, 1; Chabrié, *Ann. Chim. Phys.*, 1890, [vi], **20**, 202; Taboury, *Ann. Chim. Phys.*, 1908, [viii], **15**, 1; Wuyts, *Bull. Soc. chim.*, 1909, [iv], **5**, 405; Tschugaeff, *Ber.*, 1909, **42**, 49; Doughty, *Amer. Chem. J.*, 1909, **41**, 326. These papers also give full references to earlier work.)

In a preliminary note (*Proc.*, 1908, **24**, 134) we have shown how the method employed by Price and Twiss (*Trans.*, 1907, **91**, 2021, and succeeding papers) for the preparation of disulphides could be extended to the preparation of diselenides. A solution of sodium selenosulphate was obtained by digesting selenium with a solution of sodium sulphite and filtering from the undissolved selenium. On adding this solution to an alcoholic solution of benzyl chloride, a turbid liquid was obtained, which, however, soon cleared when heated on a water-bath under reflux. After a short

time a small quantity of a yellow oil separated, which, after removal from the remainder of the liquid, solidified on cooling; this was proved to be benzyl diselenide. Further quantities of the diselenide could be obtained from the mother liquor, either by electrolysis in a divided cell, or by the addition of sodium carbonate.

In the course of further work, an attempt was made to extend the above method to the preparation of the nitrobenzyl diselenides. It was found, however, that the solution obtained on heating sodium selenosulphate with *p*-nitrobenzyl chloride was very unstable. After a very short time, decomposition took place with the separation of much selenium, and it was only with great difficulty that the diselenide could be isolated. Various changes in the method of procedure were tried, but without success. Even when the heating was stopped as soon as the contents of the flask had become clear, and the solution rapidly cooled, decomposition took place after a time. The difficulty was finally overcome by using potassium sulphite in place of sodium sulphite. Rathke (*J. pr. Chem.*, 1865, 95, 8) found that potassium selenosulphate is more stable in solution than the corresponding sodium salt, and this is apparently true for the alkyl derivatives of these salts.

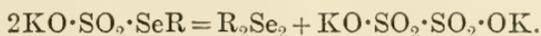
The method of procedure when potassium sulphite was used was similar to that already indicated with sodium sulphite. The use of this salt had the further result that the various potassium alkyl selenosulphates were readily isolated. When the turbid liquid, which resulted from mixing the solution of potassium selenosulphate and the alcoholic solution of the alkyl chloride, was heated over a flame under reflux, the contents of the flask cleared in two or three minutes, and, after a few minutes longer, a precipitate of the potassium alkyl selenosulphate began to form. The reaction between the potassium selenosulphate and the alkyl halide is complete in a very short time, and consequently the heating was not continued for longer than ten minutes.* At the end of that time the contents of the flask were rapidly cooled, with the result that the precipitate of the alkyl selenosulphate became much more bulky—at all events, in the case of the nitrobenzyl derivatives. This precipitate always contained some diselenide mixed with it, especially in the case of the benzyl compound. In our preliminary note we stated that this was probably formed according to the equation:



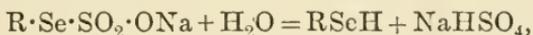
since some sulphur dioxide was evolved at the same time, but we are now of the opinion that this does not represent the true course

* Prolonged heating, even with the potassium compounds, brought about decomposition with the liberation of selenium.

of the reaction. Bunte (*Ber.*, 1874, 7, 646) and Purgotti (*Gazzetta*, 1890, 20, 25) have shown that the alkyl thiosulphates undergo thermal decomposition with the formation of disulphides and dithionate, and it has also been noticed by one of us, in conjunction with Mr. D. F. Twiss, that solutions of sodium benzyl thiosulphate become cloudy on prolonged heating, the cloudiness being caused by the formation of benzyl disulphide. The selenium compounds are less stable than the corresponding sulphur compounds, and consequently thermal decomposition takes place to a greater extent, as represented by the equation:

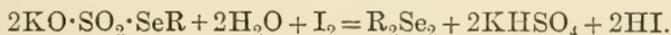


The evolution of sulphur dioxide was only noticed in the preparation of benzyl diselenide, and then only when sodium selenosulphate was used. Its formation was probably due to hydrolysis of the sodium benzyl selenosulphate by water,



and the subsequent action of the sodium hydrogen sulphate on the excess of sulphite present, or on the dithionate resulting from the thermal decomposition.

The mother liquor remaining after the precipitate of the potassium alkyl selenosulphate had been collected still contained considerable quantities of that compound. It was not recovered as such, but the diselenide was prepared from it in one of two ways. The most general method was by the action of iodine, dissolved either in alcohol or in potassium iodide solution, at the ordinary temperature. The reaction takes place very quickly, and proceeds quantitatively according to the equation:



The second method was by electrolytic reduction in a divided cell, after potassium hydrogen carbonate had been added to the solution (compare Price and Twiss, *Trans.*, 1907, 91, 2021). It is noteworthy that not only could benzyl diselenide be prepared by the electrolytic method, but also *p*- and *m*-nitrobenzyl diselenides, whereas the corresponding nitrobenzyl disulphides could not be obtained in this way (compare *Trans.*, 1908, 93, 1401). The *o*-nitrobenzyl diselenide could only be prepared by the iodine method; electrolysis led to the deposition of selenium, no diselenide being formed, probably because of steric hindrance, as was pointed out in the case of the corresponding *o*-disulphide.

All the selenium which passes into solution to form selenosulphate is recovered, either as the potassium alkyl selenosulphate or in the form of diselenide; that is, the yields obtained, as far as the

selenium is concerned, are quantitative. We have not investigated the respective yields of the alkyl selenosulphates and the diselenides.

The melting points of the diselenides prepared are given in the following table, and, for comparison, those of the corresponding disulphides:

	Diselenides.	Disulphides.
Benzyl.....	92—93°	71°
<i>o</i> -Nitrobenzyl.....	103·5	109·5
<i>m</i> -Nitrobenzyl	106·0	103·0
<i>p</i> -Nitrobenzyl	107·5	126·5

It will be seen that in the case of the diselenides the substitution of the benzyl by the nitrobenzyl group has a considerably less effect than in the disulphides, and also that the influence of the position of the nitro-group is not so marked. Moreover, *m*-nitrobenzyl diselenide has a higher melting point than the corresponding ortho-compound, whereas in the case of the disulphides the order is reversed. It is also noteworthy that, although the substitution of sulphur by selenium raises the melting point of the benzyl compounds by 21—22°, the melting point of the *m*-nitrobenzyl compound is only raised by 3°, while the melting points of the *o*- and *p*-nitrobenzyl compounds are lowered by 6° and 19° respectively.

The potassium nitrobenzyl selenosulphates are much more easily prepared than potassium benzyl selenosulphate, since they are much less soluble in water. In this respect they are very similar to the corresponding thiosulphates (Price and Twiss, *Trans.*, 1908, **93**, 1401). All the selenosulphates and diselenides prepared are more or less slowly acted on by light, with the liberation of selenium. The benzyl compounds are the least, and the *m*-nitrobenzyl compounds the most stable.

EXPERIMENTAL.

Since the potassium nitrobenzyl selenosulphates were isolated before the corresponding benzyl compounds, they will be described first, together with the corresponding diselenides.

Potassium p-Nitrobenzyl Selenosulphate, $\text{KO}\cdot\text{SO}_2\cdot\text{Se}\cdot\text{C}_7\text{H}_6\cdot\text{NO}_2$.

2·3 Grams of finely powdered selenium were boiled with a solution of 6 grams of potassium sulphite in 50 c.c. of water for three-quarters of an hour, and the hot solution filtered* from the small amount of selenium remaining undissolved; 5 grams of *p*-nitrobenzyl

* In most cases the filtrate remained clear on cooling to the ordinary temperature, but sometimes there was a very slight precipitate of selenium, which, however, did not affect the further treatment with the alkyl chloride, as it immediately disappeared on warming. When sodium sulphite was used in the place of potassium sulphite, much selenium was precipitated as soon as the solution was cooled.

chloride, dissolved in 50 c.c. of alcohol (95 per cent.), were then added, and the resulting turbid solution was heated over the free flame under reflux. The turbidity disappeared in a very short time, but after about five minutes a precipitate began to form. The heating was continued for ten minutes,* and then the contents of the flask rapidly cooled. A copious precipitate, consisting chiefly of potassium *p*-nitrobenzyl selenosulphate, but containing also small quantities of *p*-nitrobenzyl diselenide and some potassium chloride, sulphate, and sulphite, was thereby produced. The inorganic salts were eliminated by recrystallising the precipitate several times from 95 per cent. alcohol. The traces of diselenide remaining were then removed by well shaking the recrystallised substance several times with ether, leaving the pure potassium *p*-nitrobenzyl selenosulphate.

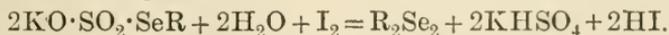
Potassium p-nitrobenzyl selenosulphate crystallises in plates, which are fairly soluble in water. In the bulk, the salt possesses a slight creamy tinge. On exposure to diffused daylight for some days, it is decomposed, with the liberation of selenium. The solution gives no precipitate with barium chloride; with sodium carbonate or sodium hydroxide, a yellow precipitate of the diselenide is produced. Hydrochloric acid gives a yellow precipitate, which consists of a mixture of the seleno-mercaptan and the diselenide; the precipitate forms slowly in the cold, but more quickly on warming. An alcoholic solution of iodine, or a solution of iodine in potassium iodide, gives an immediate precipitate of the diselenide.

The attempts to analyse this salt by estimating the potassium as sulphate were not very satisfactory. When heated very gently, either alone or after the addition of sulphuric acid, decomposition took place very rapidly with the liberation of selenium, and it was very difficult to regulate the decomposition so that no loss of salt occurred. It was found that the best method of procedure was to heat the salt alone until decomposition was complete, and then treat the residue with concentrated sulphuric acid. The potassium sulphate so obtained did not contain any selenium:

0.9144 gave 0.2342 K_2SO_4 . $K=11.49$.

$C_7H_6O_5NSKSe$ requires $K=11.69$ per cent.

The most satisfactory method of analysis was one which depended on oxidation with iodine, which, as already indicated, takes place according to the equation:



The method of procedure was as follows. A weighed amount of the salt was dissolved in water and a slight excess of iodine in

* In the first experiment in which potassium sulphite was used, the heating was continued for a longer time. After about twenty minutes the contents of the flask suddenly became red, owing to the copious deposition of selenium.

potassium iodide solution added. There was an immediate precipitate of the diselenide, and the end of the reaction was indicated by the rapid settling of the precipitate. The reaction was hastened by warming to a temperature of about 45° after the iodine had been added. The diselenide was collected, and well washed with hot water in order to remove all acid present. The iodine in the filtrate was then removed by careful addition of sodium thiosulphate, and the acid determined by titration with standard alkali. From the amount of acid liberated during the reaction, the percentage of potassium could be calculated. It was not found practicable to carry out the estimation by determining the amount of iodine used in the oxidation:

0.7531, after oxidation, required 33.03 c.c. of 0.1366*N*-NaOH.
 $K = 11.71$.

$C_7H_6O_5NSKSe$ requires $K = 11.69$ per cent.

p-Nitrobenzyl Diselenide, $(NO_2 \cdot C_6H_4 \cdot CH_2)_2Se_2$.

This was prepared from the filtrate and mother liquors obtained in the preparation and recrystallisation of the potassium *p*-nitrobenzyl selenosulphate. An alcoholic solution of iodine was added until the colour of the iodine persisted, and then water, in order to precipitate the last traces of diselenide from the alcoholic solution. The diselenide was then recrystallised from alcohol, a drop of sulphurous acid being added to remove any iodine.

In one experiment the filtrate obtained in the preparation of potassium *p*-nitrobenzyl selenosulphate was electrolysed at the cathode in a divided cell (compare Price and Twiss, *Trans.*, 1907, **91**, 2021), after the addition of 6 grams of potassium hydrogen carbonate. A rotating cathode (area = 0.5 sq. dcm.) was used, and 0.25 ampere passed for one hour, and 0.5 ampere for another hour. A copious precipitate of the diselenide was formed. The filtrate from this precipitate, on standing in the dark overnight, gave a deposit of selenium. This was collected, and the filtrate again electrolysed, but there was only a further deposit of selenium.

It was also proved that the precipitate formed by the addition of sodium carbonate to an aqueous solution of potassium *p*-nitrobenzyl selenosulphate consists of the diselenide, but it is not as pure as that obtained by iodine oxidation or by electrolysis.

p-Nitrobenzyl diselenide, on recrystallisation from alcohol, gives a felted mass of canary-yellow crystals, which melt at 107.5° . On exposure to diffused daylight for some days it gradually turns red, owing to the liberation of selenium. With alcoholic sodium hydroxide it gives no immediate colour in the cold, but

a deep red colour on warming (compare the corresponding disulphide, *Trans.*, 1908, **93**, 1401).

The selenium was determined by the method of Frerichs (*Arch. Pharm.*, 1902, **240**, 656):

0.3218 required 29.63 c.c. *N*/10-potassium thiocyanate. Se = 36.46.

0.2051 gave 12.10 c.c. N_2 (moist) at 17° and 739 mm. N = 6.62.

$C_{14}H_{12}O_4N_2Se_2$ requires Se = 36.79; N = 6.51 per cent.

Potassium m-Nitrobenzyl Selenosulphate.

This was prepared from *m*-nitrobenzyl chloride in a similar way to the corresponding para-compound, using the same quantities of reagents. It crystallises in colourless plates, which are fairly readily soluble in water, and are more readily obtained pure than the para-compound. Selenium is liberated on exposure to light:

0.5137, after oxidation, required 22.51 c.c. of 0.1366*N*-NaOH.

K = 11.70.

$C_7H_6O_5NSKSe$ requires K = 11.69 per cent.

m-Nitrobenzyl Diselenide.

This was obtained from the *m*-nitrobenzyl selenosulphate by oxidation with iodine, in a similar manner to that already described for the *p*-diselenide. It could also be prepared by electrolytic reduction of the selenosulphate. It crystallises from alcohol in flat needles, which possess only a very faint yellow tinge, and melt at 106°. It is much more stable towards diffused daylight than the *p*-diselenide, but on prolonged exposure it gradually acquires a red tinge. With alcoholic sodium hydroxide it gives a red colour on warming:

0.3050 required 28.55 c.c. *N*/10-potassium thiocyanate. Se = 37.08.

0.3868 gave 23.20 c.c. N_2 (moist) at 19.2° and 734.9 mm. N = 6.62.

$C_{14}H_{12}O_4N_2Se_2$ requires Se = 36.79; N = 6.51 per cent.

Potassium o-Nitrobenzyl Selenosulphate.

This is prepared in a similar manner to the para- and meta-compounds, and possesses similar properties. It crystallises from alcohol in colourless plates:

0.4423, after oxidation, required 19.40 c.c. of 0.1366*N*-NaOH.

K = 11.72.

$C_7H_6O_5NSKSe$ requires K = 11.69 per cent.

o-Nitrobenzyl Diselenide.

This was prepared from the potassium *o*-nitrobenzyl selenosulphate by oxidation with iodine, exactly as described for the para- and meta-compounds. It could not be obtained by electrolytic reduction of the selenosulphate. It crystallises from alcohol in yellow plates, which melt at 103·5°. It is about as sensitive to light as the para-compound. With alcoholic sodium hydroxide, it gives a deep red colour on warming:

0·2877 required 32·15 c.c. *N*/10-potassium thiocyanate. Se=36·85.

0·2116 gave 12·30 c.c. N₂ (moist) at 20° and 756 mm. N=6·58.

C₁₄H₁₂O₄N₂Se₂ requires Se=36·79; N=6·51 per cent.

Potassium Benzyl Selenosulphate, KO·SO₂·Se·CH₂·C₆H₅.

The solution of this substance was prepared in a similar manner to that used for the nitrobenzyl compounds, the quantities taken being 3 grams of selenium, 8 grams of potassium sulphite, 40 c.c. of water, and 40 c.c. of alcohol. Owing to the ready solubility of the salt in water, however, the quantity of precipitate which separated on cooling was very small; also, since potassium benzyl selenosulphate is much less stable than the corresponding nitrobenzyl salts, the precipitate contained a large proportion of the diselenide. In order to remove the diselenide, the solution, together with the precipitate, was extracted with ether. The aqueous layer was then evaporated to dryness over concentrated sulphuric acid in a vacuum, and the potassium benzyl selenosulphate extracted from the residue by boiling with 95 per cent. alcohol. The crystals which separated from the alcoholic extract on cooling were, however, by no means pure. In the preparation of the potassium selenosulphate, some sulphite remains unacted on by the selenium, and this, to some extent, forms potassium benzylsulphonate with the benzyl chloride. Repeated crystallisation from alcohol is necessary to purify the benzyl selenosulphate from the benzyl sulphonate.

Potassium benzyl selenosulphate crystallises in colourless plates, which are very readily soluble in water. On exposure to light, decomposition readily takes place with liberation of selenium. The solution gives no precipitate with barium chloride. Oxidation with iodine gives the diselenide, but this reaction cannot be used for the analysis of the salt, since the diselenide does not settle readily, and excess of iodine seems to facilitate decomposition, with liberation of selenium. The best method of determining the percentage of potassium is to decompose the salt by gentle heat—the decomposition does not take place violently, as in the case of the

nitrobenzyl compounds—and then treat the residue with concentrated sulphuric acid. This method is also a good test of the purity of the salt. If it is quite pure, heating alone gives potassium sulphate, the weight of which is not altered by treatment with sulphuric acid, whereas, if potassium benzylsulphonate is present, the residue left after heating contains potassium sulphite:

0.3024 gave 0.3189 CO_2 and 0.0764 H_2O . C = 28.76; H = 2.83.

0.5017 „ 0.1521 K_2SO_4 . K = 13.60.

$\text{C}_7\text{H}_7\text{O}_3\text{SKSe}$ requires C = 29.02; H = 2.44; K = 13.51 per cent.

Benzyl Diselenide, $(\text{C}_6\text{H}_5\cdot\text{CH}_2)_2\text{Se}_2$.

This was prepared from potassium benzyl selenosulphate, either by oxidation with iodine, or by electrolytic reduction. For the first method, the alcoholic mother liquors obtained in the recrystallisation of the potassium benzyl selenosulphate were generally used. After excess of iodine had been added, the diselenide remaining in solution was precipitated by the addition of water. It was collected immediately and recrystallised from alcohol, since, as has already been pointed out, the presence of iodine seemed to facilitate the decomposition, with liberation of selenium. When recrystallising, a drop of sulphurous acid was added to remove any iodine present, and it was also necessary to wash the crystals well with water to remove any traces of hydriodic acid before they were dried.

For the electrolytic method, an aqueous solution of potassium benzyl selenosulphate was used, the method of procedure being similar to that described for *p*-nitrobenzyl diselenide. The strength of current was 0.25 to 0.5 ampere.

Benzyl diselenide crystallises from alcohol in yellow needles, which are slightly deeper in colour than those of *p*-nitrobenzyl diselenide, and melt at 92—93°. Jackson (*Annalen*, 1875, **179**, 1) describes the crystals as lustrous, yellow plates, melting at 90°. It is possible that the compound he obtained was not quite pure, since we have found that the slightly impure crystals have properties agreeing with those described by Jackson, even to the melting point. This is especially the case when the crystals are obtained from a concentrated alcoholic solution.

Benzyl diselenide is very sensitive to light as compared with the nitrobenzyl compounds. An exposure of an hour or so to diffused daylight turns it red:

0.2122 required 24.77 c.c. *N*/10-potassium thiocyanate. Se = 46.2.

$\text{C}_{14}\text{H}_{14}\text{Se}_2$ requires Se = 46.5 per cent.

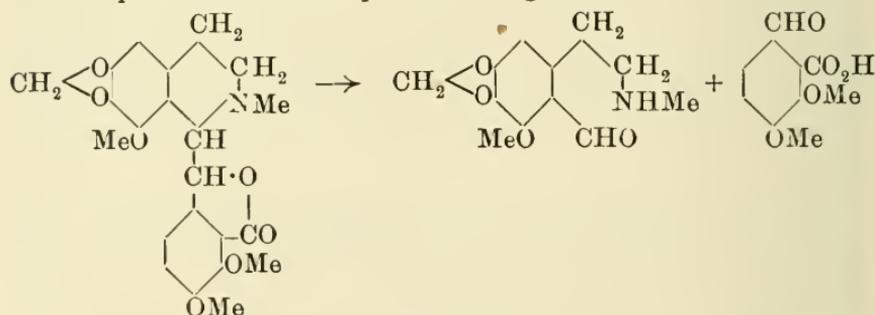
We desire to express our thanks to the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the expenses of the foregoing investigation.

CHEMICAL DEPARTMENT,
MUNICIPAL TECHNICAL SCHOOL,
BIRMINGHAM.

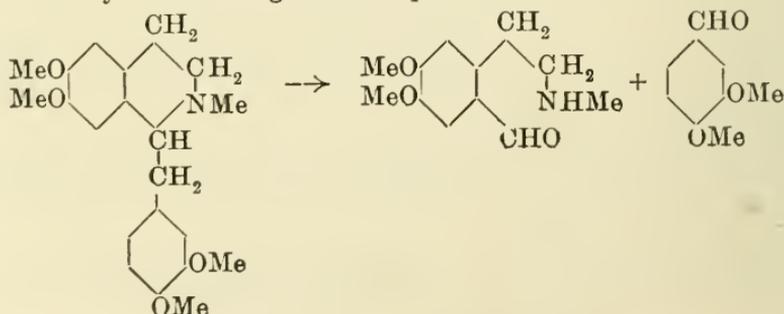
CXCI.—*isoQuinoline Derivatives. Part III. The Oxidation of Substituted 1-Benzyltetrahydroisoquinolines.*

By FRANK LEE PYMAN.

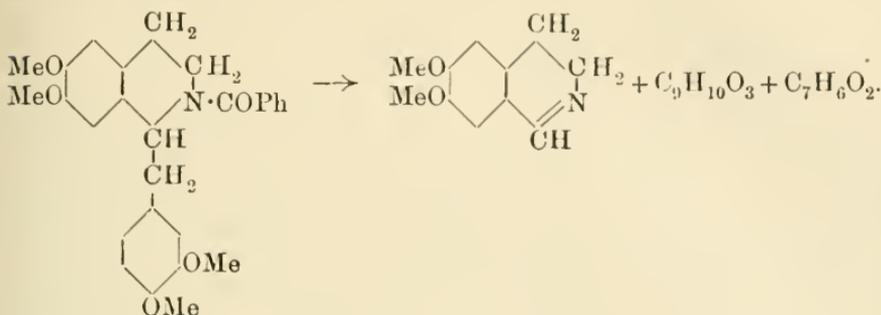
IT has long been known that narcotine and hydrastine yield, on oxidation with manganese dioxide and sulphuric acid, opianic acid and cotarnine and hydrastinine respectively. The following scheme represents the degradation of narcotine to cotarnine; hydrastine differs only from narcotine in being devoid of the methoxy-group in the 8-position of the *isoquinoline* ring:



The author has recently shown (this vol., pp. 1266 and 1610) that laudanosiine is also amenable to the same type of degradation, yielding 4:5-dimethoxy-2- β -methylaminoethylbenzaldehyde and veratraldehyde according to the equation:



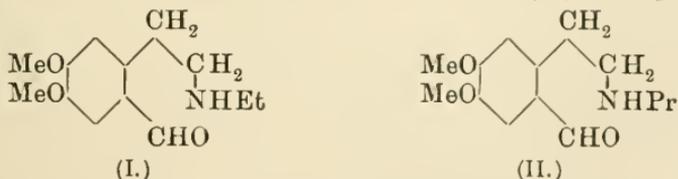
whilst *N*-benzoyltetrahydropapaverine gives rise, under similar conditions, to 6:7-dimethoxy-3:4-dihydroisoquinoline, veratraldehyde, and benzoic acid:



It was thus shown that this method of oxidation is applicable to the cleavage, not only of 1-opianyltetrahydroisoquinolines, that is to say, of compounds in which the carbon atom joining the isoquinoline and benzene rings is already partly oxygenated, but also of certain 1-veratryltetrahydroisoquinolines, compounds in which the two rings are connected by a methylene group.

In view of these results, it seemed desirable to apply this method of oxidation to a further number of substances of similar constitution to those already investigated, with the view of determining the scope of its application in respect of the nature of the substituent groups. Furthermore, it seemed likely that the method might be capable of somewhat general application, and consequently of value in the elucidation of the constitution of a number of naturally occurring alkaloids of at present undetermined structure. This refers particularly to some of the rarer opium alkaloids, with regard to which there is strong reason to believe that they are substituted 1-benzyltetrahydroisoquinolines.

N-Ethyltetrahydropapaverine and *N*-propyltetrahydropapaverine, when oxidised with manganese dioxide and sulphuric acid, undergo the same type of change as does laudanosine, yielding veratraldehyde and 4:5-dimethoxy-2- β -ethylaminoethylbenzaldehyde (I) and 4:5-dimethoxy-2- β -propylaminoethylbenzaldehyde (II) respectively;

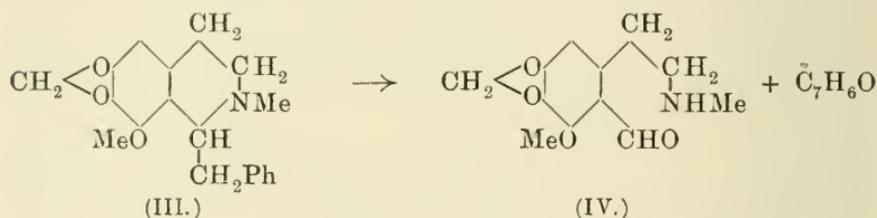


these compounds and a number of derivatives, of which details will be found in the experimental part of this paper, behave similarly to the corresponding methyl homologues obtained from laudanosine. Further, tetrahydropapaverine, like its

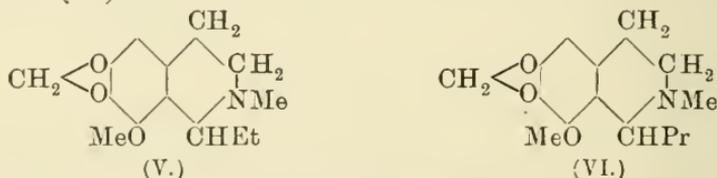
N-benzoyl derivative, yields on oxidation 6:7-dimethoxy-3:4-dihydroisoquinoline and veratraldehyde. It is therefore clear that the course of this reaction is uninfluenced by the character of the side-chain attached to the nitrogen atom, since this may be either a hydrogen atom, an alkyl or an acyl group.

It must be remarked that up to this point, in the case of all those substances which have undergone the type of change instanced, the substituent in the 1-position has been either the opianyl (narcotine, hydrastine) or the veratryl residue (tetrahydropapaverine derivatives). It therefore seemed of interest to apply this oxidation to bases containing other groups in this position in order to determine whether the presence of a benzyl group was an essential factor. For this purpose, 1-benzylhydrocotarnine and the 1-alkylhydrocotarnines, which are readily prepared by Freund and Reitz's method (*Ber.*, 1906, **39**, 2219), appeared to be suitable.

It was found that 1-benzylhydrocotarnine (III) readily underwent the same type of change as in the cases previously instanced, yielding cotarnine (IV) and benzaldehyde:

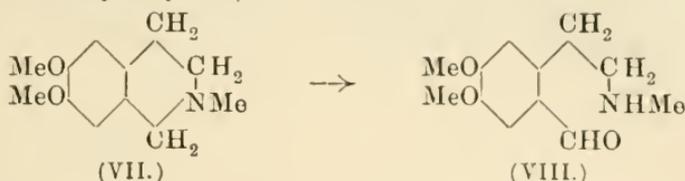


On the other hand, 1-ethylhydrocotarnine (V) and 1-propylhydrocotarnine (VI):



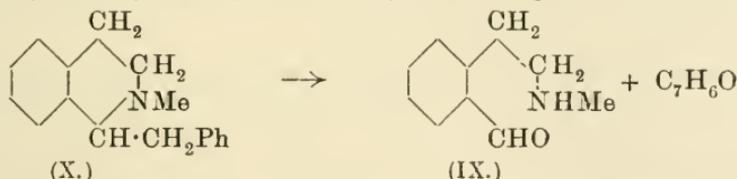
after oxidation under similar conditions, were to a large extent recovered unaltered, and cotarnine could not be isolated from the products of the reaction. It would, therefore, appear that the presence of a benzyl group in the 1-position is an essential factor for the cleavage under these conditions of substituted tetrahydroisoquinolines containing a hydrocarbon substituent in the 1-position. In this connexion, it is interesting to note, however, that in certain cases, where there is no substituent in the 1-position, substituted 2-alkyltetrahydroisoquinolines readily yield the corresponding substituted 2- β -alkylaminoethylbenzaldehydes on oxidation; thus, hydrocotarnine yields cotarnine, hydrohydrastinine yields hydrastinine, and it has now been found that 6:7-dimethoxy-2-methyltetra-

hydroisoquinoline (VII) yields 4 : 5-dimethoxy-2- β -methylaminoethylbenzaldehyde (VIII):



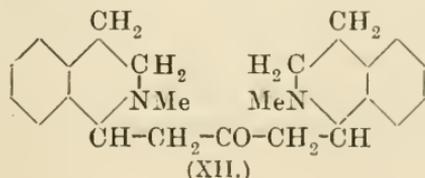
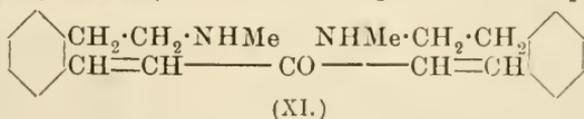
The formation of cotarnine in this manner led Freund and Beck (*Ber.*, 1904, **37**, 1942) to attempt the preparation of 2- β -methylaminoethylbenzaldehyde by the oxidation of 2-methyltetrahydroisoquinoline; they did not, however, obtain this compound, but a higher oxidation product, 1 : 3 : 4-triketo-2-methyltetrahydroisoquinoline.

In view of the general nature of the results obtained by the oxidation of 1-benzyltetrahydroisoquinolines, it appeared probable, however, that 2- β -methylaminoethylbenzaldehyde (IX) would be obtained, together with benzaldehyde, on the oxidation of 1-benzyl-2-methyltetrahydroisoquinoline (X), and this proved to be the case:

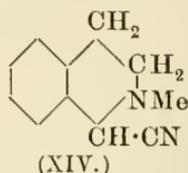
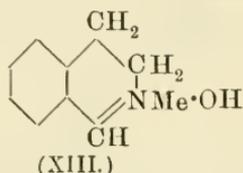


The latter reaction is of special interest, since 1-benzyl-2-methyltetrahydroisoquinoline, which has recently been described by Freund and Bode (*Ber.*, 1909, **42**, 1763), is the parent substance of a number of alkaloids, for instance, narcotine, hydrastine, and laudanose, whilst 2- β -methylaminoethylbenzaldehyde is the parent substance of their degradation products, cotarnine, hydrastinine, and 4 : 5-dimethoxy-2- β -methylaminoethylbenzaldehyde respectively.

2- β -Methylaminoethylbenzaldehyde possesses properties, for the most part, similar to those of the alkyloxy-substituted 2- β -methylaminoethylbenzaldehydes; for instance, it readily yields an *acetone condensation product* (XI or XII; compare this vol., p. 1268), and



forms salts of 2-methyl-3:4-dihydroisoquinolinium hydroxide (XIII) by substitution; further, aqueous solutions of its salts yield, with potassium cyanide, 1-cyano-2-methyltetrahydroisoquinoline (XIV), a compound insoluble in water, but soluble in ether:



2- β -Methylaminoethylbenzaldehyde is, however, a weaker base than the corresponding alkyloxy-substituted derivatives, for it can be slowly extracted by solvents from aqueous solutions after the addition of sodium carbonate, although much more readily after the addition of sodium hydroxide, whereas the alkyloxy-substituted bases can only be extracted after the addition of the latter. Its salts, the 2-methyl-3:4-dihydroisoquinolinium salts, differ in an interesting particular from the alkyloxy-substituted 2-methyl-3:4-dihydroisoquinolinium salts, for the chloride is colourless, and the aurichloride golden, whilst in the latter salts the chlorides are primrose and the aurichlorides brown.

2-Methyl-3:4-dihydroisoquinolinium iodide is bright yellow, but yields a colourless, aqueous solution, behaving in this respect like many other substituted ammonium iodides (compare Decker, *Ber.*, 1904, **37**, 3938).

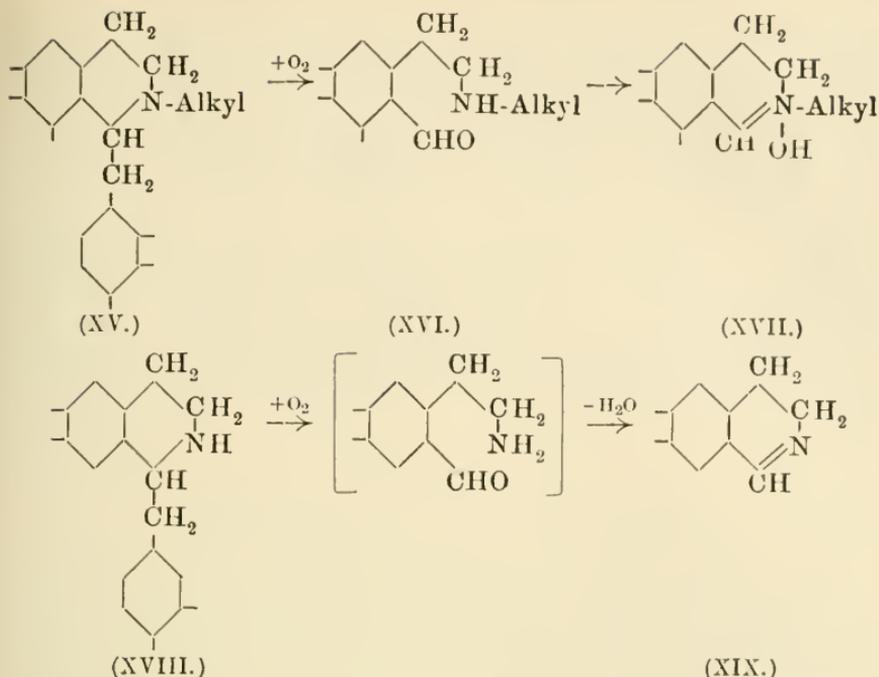
It has previously been observed that *N*-benzoyl-1:2-dihydropapaverine does not undergo the same type of change on oxidation as does *N*-benzoyltetrahydropapaverine, and it has now been found that 1:2-dihydropapaverine is similarly stable.

The evidence afforded by the results of the oxidation of substituted tetrahydroisoquinolines given in this and the two preceding papers appears to justify the following general conclusions.

1. That substituted 1-benzyltetrahydroisoquinolines suffer oxidation and fission simultaneously under the influence of hot dilute sulphuric acid and manganese dioxide, yielding the aldehyde corresponding with the substituted benzyl group, and a basic degradation product.

2. That in the case of substituted 1-benzyl-2-alkyltetrahydroisoquinolines (XV), the basic product is a substituted 2- β -alkylaminoethylbenzaldehyde (XVI), which yields salts of the corresponding 2-alkyl-3:4-dihydroisoquinolinium hydroxide (XVII).

3. That in the case of substituted 1-benzyl-2-acyltetrahydroisoquinolines, and 1-benzyltetrahydroisoquinolines containing a free imino-group (XVIII), the basic product is a substituted 3:4-dihydroisoquinoline (XIX):



4. That substituted 1-alkyltetrahydroisoquinolines do not undergo this reaction.

In conclusion, the following short account of the physiological properties of certain isoquinoline derivatives described above or in the preceding papers may be of interest. The physiological examination of these compounds has been carried out by Dr. H. H. Dale and Mr. P. P. Laidlaw, of the Wellcome Physiological Research Laboratories, to whom the author wishes to express his best thanks.

6: 7-Dimethoxy-2-methyl-3: 4-dihydroisoquinolinium chloride (A), 6: 7-dimethoxy-2-ethyl-3: 4-dihydroisoquinolinium chloride (B), 2-methyl-3: 4-dihydroisoquinolinium iodide (C), and 6: 7-dimethoxy-2-methyltetrahydroisoquinoline hydrochloride (D), all have an action on the isolated uterus similar to that of cotarnine. 6: 7-Dimethoxy-3: 4-dihydroisoquinoline hydrochloride (E) has very little action in this respect.

In their action on the blood-pressure, "B" and "D" are most like cotarnine, causing a fall, succeeded by a very slight rise. "A" causes a distinct rise of pressure, due to vaso-constriction. It is uncertain as yet whether this vaso-constriction is central or peripheral in origin, but the probability is in favour of the former. It renders the heart-beat at the same time slower and stronger. This last action is definitely peripheral, as it can be observed in

the isolated, perfused heart. "E" is more depressant than any of the others, causing a marked weakening of the heart's action. "C" is peculiar in the group, in that it causes, in doses of 10 to 20 milligrams, a marked rise of blood-pressure superficially similar to that produced by adrenine. Whether the action is really of that kind cannot be decided without further experiment.

The general toxicity of these compounds has been also investigated. "A" and "B" act in this respect much like cotarnine, but are more toxic, "A" being about one and a-half times and "B" twice as toxic as cotarnine for the guinea-pig. "D" and "E" are convulsant poisons, and, of the two, "D" causes the more marked convulsions, but "E" is lethal in smaller doses.

EXPERIMENTAL.

N-Ethyltetrahydropapaverine, $C_{22}H_{29}O_4N$.

One hundred grams of papaverine, 50 grams of ethyl iodide, and 250 grams of absolute alcohol were boiled on the water-bath for ten hours under a reflux condenser. The solvents were then distilled off, and left a bright yellow, crystalline mass of crude papaverine ethiodide, which melted at 180—200°. Without further purification, this was dissolved in 1.7 litres of boiling water, and stirred for fifteen minutes with 47 grams of freshly precipitated silver chloride. After filtration, the liquor was concentrated to a thick syrup, which was then mixed with 400 c.c. of concentrated hydrochloric acid and 400 c.c. of alcohol, and digested on the water-bath with 200 grams of tin for sixteen hours. The liquor was next decanted from undissolved tin, evaporated to remove the alcohol, and then diluted with water. This caused the separation of a putty-like tin salt, which was collected, dissolved in 3 litres of boiling water, and decomposed by a stream of hydrogen sulphide. The liquor was then filtered, cooled, and mixed with an excess of 10 per cent. aqueous sodium hydroxide. The base, which first separated as an oil, readily became crystalline, and was collected and well washed with cold water; the yield amounted to 66 grams, that is, 60 per cent. of the theoretical.

N-Ethyltetrahydropapaverine crystallises from absolute alcohol in white, fluffy needles, which melt at 89° (corr.). It is insoluble in water, and somewhat sparingly soluble in cold alcohol:

0.1582 gave 0.4102 CO_2 and 0.1105 H_2O . C=70.7; H=7.8.

0.1421 ,, 4.7 c.c. N_2 at 17° and 762 mm. N=3.9.

$C_{22}H_{29}O_4N$ requires C=71.1; H=7.9; N=3.8 per cent.

The *picrate* crystallises from alcohol in yellow, monoclinic prisms

with a macrodome, and melts at 167—170° (corr.). It is anhydrous, and is sparingly soluble in water or cold alcohol :

0·1543 gave 0·3166 CO₂ and 0·0778 H₂O. C=56·0; H=5·7.

0·1423 „ 11·0 c.c. N₂ at 19° and 770 mm. N=9·2.

C₂₂H₂₉O₄N₃ requires C=56·0; H=5·4; N=9·3 per cent.

4 : 5-Dimethoxy-2-β-ethylaminoethylbenzaldehyde (I, p. 1739).

This base was prepared by the oxidation of *N*-ethyltetrahydropapaverine. Since the method employed was precisely similar to that used for the preparation of 4 : 5-dimethoxy-2-β-methylaminoethylbenzaldehyde from laudanoline, a detailed description of it is unnecessary.

Sixty grams of *N*-ethyltetrahydropapaverine gave, on oxidation with 36 grams of pyrolusite, containing 80 per cent. of manganese dioxide, in dilute sulphuric acid solution, 28 grams of 6 : 7-dimethoxy-2-ethyl-3 : 4-dihydroisoquinolinium chloride, that is, 59 per cent. of the theoretical.

The base separates as an oil on the addition of 50 per cent. aqueous sodium hydroxide to a concentrated aqueous solution of the chloride, but has not been obtained in a crystalline form. It combines with acids, forming salts by substitution of the isomeric 6 : 7-dimethoxy-2-ethyl-3 : 4-dihydroisoquinolinium hydroxide.

The chloride crystallises from a mixture of one part of absolute alcohol and 9 parts of absolute ethyl acetate in bunches of broad, yellow, glistening needles, which contain 2 molecules of water of crystallisation, and melt at 91—92° (corr.). After drying at 100°, this salt decomposes at about 190° (corr.). It is easily soluble in water or alcohol, giving neutral yellow solutions, which show a beautiful blue fluorescence when sufficiently diluted :

0·1797, air-dried salt, gave 0·3510 CO₂ and 0·1218 H₂O. C=53·3; H=7·6.

0·6511, air-dried salt, lost 0·0812 at 100°. H₂O=12·5.

C₁₃H₁₈O₂NCl·2H₂O requires C=53·5; H=7·6; H₂O=12·4 per cent.

0·1590, dried at 100°, gave 0·3557 CO₂ and 0·1018 H₂O. C=61·0; H=7·2.

0·1421, dried at 100°, gave 0·0809 AgCl. Cl=14·1.

C₁₃H₁₈O₂NCl requires C=61·0; H=7·1; Cl=13·9 per cent.

The aurichloride crystallises from absolute alcohol in chestnut-brown, serrated needles, which melt at 138—139° (corr.). It is anhydrous, and is very sparingly soluble in water or cold alcohol :

0·1865 gave 0·0658 Au. Au=35·3.

C₁₃H₁₈O₂NCl₄Au requires Au=35·3 per cent.

The *picrate* crystallises from alcohol in hard, yellow, glistening rods, which melt at 139—140° (corr.).

4:5-Dimethoxy-2- β -ethylaminoethylbenzaldehyde behaves similarly to its methyl homologue; thus, it is converted into 1-keto-6:7-dimethoxy-2-ethyltetrahydroisoquinoline and 6:7-dimethoxy-2-ethyltetrahydroisoquinoline by the action of hot aqueous sodium hydroxide, and yields bis-(4:5-dimethoxy-2- β -ethylaminoethylbenzylidene)acetone when dissolved in dilute aqueous sodium hydroxide and mixed with acetone.

1-Keto-6:7-dimethoxy-2-ethyltetrahydroisoquinoline, $C_{13}H_{17}O_3N$.

This compound crystallises from a mixture of xylene and light petroleum in large, colourless, monoclinic plates, which melt at 95° (corr.). Its solubilities and chemical properties are similar to those of the methyl homologue:

0.1517 gave 0.3703 CO_2 and 0.0994 H_2O . C = 66.5; H = 7.3.

0.1580 ,, 8.3 c.c. N_2 at 14° and 752 mm. N = 6.2.

$C_{13}H_{17}O_3N$ requires C = 66.3; H = 7.3; N = 6.0 per cent.

6:7-Dimethoxy-2-ethyltetrahydroisoquinoline, $C_{13}H_{19}O_2N$.

This compound is purified by crystallisation of the hydrochloride, regeneration from the pure salt, and distillation under diminished pressure.* It distils at 218°(corr.)/37 mm. as a colourless oil, which slowly solidifies. On crystallisation from light petroleum, this base separates in clusters of prismatic needles, which melt at 34—35° (corr.). It is readily soluble in cold water, but very sparingly so in boiling water, and is very easily soluble in all the usual organic solvents at the ordinary temperature, but sparingly so in light petroleum at 0°:

0.1546 gave 0.3979 CO_2 and 0.1206 H_2O . C = 70.2; H = 8.7.

$C_{13}H_{19}O_2N$ requires C = 70.5; H = 8.7 per cent.

The *hydrochloride* crystallises from moist ethyl acetate in short, white needles, which are anhydrous, and melt at 237—239° (corr.). It is readily soluble in water or alcohol:

0.1474 gave 0.3260 CO_2 and 0.1048 H_2O . C = 60.3; H = 8.0.

0.1485 ,, 0.0819 AgCl. Cl = 13.7.

$C_{13}H_{19}O_2N, HCl$ requires C = 60.5; H = 7.8; Cl = 13.8 per cent.

* 6:7-Dimethoxy-2-methyltetrahydroisoquinoline distils at 210°(corr.)/40 mm.; this base is readily oxidised to 4:5-dimethoxy-2- β -methylaminoethylbenzaldehyde by cold dilute chromic acid.

Bis-(4 : 5-dimethoxy-2-β-ethylaminoethylbenzylidene)acetone,
 $C_{29}H_{40}O_5N_2$.

The base was obtained as a colourless oil, which did not crystallise. The *dihydrochloride* separates as a white, crystalline powder when a solution of the base in acetone is neutralised with concentrated hydrochloric acid, and has been obtained in two hydrated forms with 1 and $2\frac{1}{2}$ molecular proportions of water of crystallisation. It readily yields 6 : 7-dimethoxy-2-ethyl-3 : 4-dihydroisoquinolinium chloride when heated with water, but on dissolving it quickly in boiling water and cooling immediately, a small proportion separates again as a crystalline powder, which decomposes, becoming orange in colour at about 197° (corr.). It is very sparingly soluble in cold water or alcohol:

0·5368, air-dried, lost 0·0149 at 100° . $H_2O = 2\cdot8$.

0·2377 „ „ 0·0183 „ 100° . $H_2O = 7\cdot7$.

$C_{29}H_{40}O_5N_2, 2HCl, H_2O$ requires $H_2O = 3\cdot1$ per cent.

$C_{29}H_{40}O_5N_2, 2HCl, 2\frac{1}{2}H_2O$ „ $H_2O = 7\cdot3$ „

0·1612, dried at 100° , gave 0·3593 CO_2 and 0·1091 H_2O . $C = 60\cdot8$;
 $H = 7\cdot6$.

0·3503, dried at 100° , gave 0·1731 $AgCl$. $Cl = 12\cdot2$.

$C_{29}H_{40}O_5N_2, 2HCl$ requires $C = 61\cdot1$; $H = 7\cdot4$; $Cl = 12\cdot4$ per cent.

The following propyl derivatives were prepared in the same manner as the corresponding ethyl homologues.

N-Propyltetrahydropapaverine, C₂₃H₃₁O₄N.

This base was obtained in an amorphous form by the reduction of papaverine propochloride.

The *picrate* crystallises from absolute alcohol in large, irregular, yellow prisms, which melt at 122 — 125° (corr.). It is anhydrous, and is sparingly soluble in water or cold alcohol:

0·1509 gave 0·3117 CO_2 and 0·0751 H_2O . $C = 56\cdot3$; $H = 5\cdot6$.

$C_{23}H_{31}O_4N, C_6H_3O_7N_3$ requires $C = 56\cdot6$; $H = 5\cdot6$ per cent.

4 : 5-Dimethoxy-2-β-propylaminoethylbenzaldehyde (II, p. 1739).

This base was prepared by the oxidation of *N*-propyltetrahydropapaverine; it separates as an oil on the addition of 50 per cent. aqueous sodium hydroxide to a concentrated solution of the chloride, but has not been obtained in a crystalline form. It combines with acids, forming salts by substitution of the corresponding 6 : 7-dimethoxy-2-propyl-3 : 4-dihydroisoquinolinium hydroxide.

The *chloride* crystallises from a mixture of 1 part of absolute alcohol and 9 parts of ethyl acetate in clusters of small, primrose needles, which melt at 78—79° (corr.). It is easily soluble in water, giving a yellow solution, which shows a blue fluorescence when diluted. This salt contains 2 molecules of water of crystallisation, and is gradually converted into an amorphous, deliquescent gum on partial dehydration either in a vacuum over sulphuric acid or on heating:

0.1568, air-dried salt, gave 0.3122 CO₂ and 0.1099 H₂O. C=54.3;
H=7.9.

0.1768, air-dried salt, gave 0.0826 AgCl. Cl=11.6.
C₁₄H₂₀O₂NCl, 2H₂O requires C=54.9; H=7.9; Cl=11.6 per cent.

The *picrate* crystallises from alcohol in beautiful, long, deep yellow needles, which begin to sinter at 146° and melt at 148—149° (corr.). This salt is anhydrous, and is very sparingly soluble in water and sparingly so in cold alcohol:

0.1543 gave 0.2916 CO₂ and 0.0662 H₂O. C=51.5; H=4.8.
C₂₀H₂₂O₉N₄ requires C=51.9; H=4.8 per cent.

1-*Keto-6: 7-dimethoxy-2-propyltetrahydroisoquinoline*, C₁₄H₁₉O₃N.

This compound crystallises from a mixture of benzene and light petroleum in large, colourless, oblong, monoclinic plates, which begin to soften at 75°, and melt at 77° (corr.). It is easily soluble in water and the usual organic solvents, with the exception of light petroleum:

0.1515 gave 0.3727 CO₂ and 0.1042 H₂O. C=67.1; H=7.7.
C₁₄H₁₉O₃N requires C=67.4; H=7.7 per cent.

6: 7-*Dimethoxy-2-propyltetrahydroisoquinoline*, C₁₄H₂₁O₂N.

This base was obtained as a pale yellow oil which did not crystallise on keeping.

The *hydrochloride* crystallises from aqueous acetone in microscopic, fluffy needles, which melt to a yellow liquid at 224° (corr.). This salt is easily soluble in water, but sparingly so in cold alcohol. It contains half a molecular proportion of water of crystallisation, which is not entirely lost at 150°:

0.1534, air-dried salt, gave 0.3379 CO₂ and 0.1129 H₂O. C=60.1;
H=8.2.

0.1805, air-dried salt, gave 0.0940 AgCl. Cl=12.9.
C₁₄H₂₁O₂N, HCl, $\frac{1}{2}$ H₂O requires C=59.8; H=8.3; Cl=12.6 per cent.

Oxidation of 1-Benzyl-2-methyltetrahydroisoquinoline.

Eighteen grams of 1-benzyl-2-methyltetrahydroisoquinoline were dissolved in a mixture of 35 grams of concentrated sulphuric acid and 250 c.c. of water, and well stirred with 16.6 grams of pyrolusite, containing 80 per cent. of manganese dioxide, for three-quarters of an hour on a steam-bath. The mixture was then distilled in a current of steam, and the resulting distillate extracted with ether, which removed 3.3 grams of benzaldehyde; this was recognised by its characteristic odour, and by the formation of the phenylhydrazone, which melted at 158—160° (corr.). The residual liquor from the steam distillation was filtered from a quantity—perhaps 2 grams—of resinous matter, extracted with ether, which removed 1.0 gram of yellow oil, containing some benzaldehyde, rendered alkaline with sodium carbonate, and again extracted with ether, which removed a crystalline basic compound rather slowly. Sodium hydroxide solution was then added, and the extraction continued, when the same crystalline base was readily extracted. The ethereal residues from both extractions were evaporated to low bulk, and then allowed to evaporate to dryness spontaneously, when in each case the residue consisted of colourless prisms covered with a brown oil. On stirring the residues with acetone and filtering, the crystals of 2- β -methylaminoethylbenzaldehyde were obtained in an almost pure condition; the yield amounted to 5.6 grams, that is, 45 per cent. of the theoretical.

No further quantity of crystalline material could be obtained from the acetone liquors, either in the form of the base or that of a salt.

2- β -Methylaminoethylbenzaldehyde (IX, p. 1741).

This base crystallises from ether, acetone, or benzene in beautiful, colourless prisms, which melt at 110—111° (corr.). It is very sparingly soluble in water or light petroleum, sparingly so in cold acetone, fairly easily so in ether or benzene, and readily so in alcohol, ethyl acetate, or chloroform:

0.1508 gave 0.4076 CO₂ and 0.1082 H₂O. C = 73.7; H = 8.0.

0.1506 „, 11.1 c.c. N₂ at 24° and 756 mm. N = 8.4.

C₁₀H₁₃ON requires C = 73.6; H = 8.1; N = 8.6 per cent.

The base is readily soluble in dilute acids, forming salts derived by substitution from the isomeric 2-methyl-3:4-dihydroisoquinolinium hydroxide.

The chloride forms colourless crystals, which are very deliquescent, and are readily soluble in water or alcohol, but insoluble in acetone.

The *iodide* crystallises from absolute alcohol in long, bright yellow needles, which become orange, and begin to soften at about 115° , and melt at $125\text{--}128^{\circ}$ (corr.) to a red liquid. This salt is anhydrous, and is easily soluble in water, giving a colourless, neutral solution, but rather sparingly so in alcohol:

0.1527 gave 0.2459 CO_2 and 0.0605 H_2O . C=43.9; H=4.4.

$\text{C}_{10}\text{H}_{12}\text{NI}$ requires C=43.9; H=4.4 per cent.

The *aurichloride* crystallises from absolute alcohol in bright golden, feathery needles, which melt at 145° (corr.). It is very sparingly soluble in water or cold alcohol, and is anhydrous:

0.1822 gave 0.1672 CO_2 and 0.0435 H_2O . C=25.0; H=2.7.

0.2180 ,, 0.0888 Au. Au=40.7.

$\text{C}_{10}\text{H}_{12}\text{NCl}_4\text{Au}$ requires C=24.7; H=2.5; Au=40.6 per cent.

The *picrate* crystallises from alcohol in fine, silky, yellow needles, which melt at 145° (corr.), after previous sintering. It is sparingly soluble in water or cold alcohol:

0.1383 gave 0.2588 CO_2 and 0.0470 H_2O . C=51.0; H=3.8.

$\text{C}_{16}\text{H}_{14}\text{O}_7\text{N}_4$ requires C=51.3; H=3.8 per cent.

1-Cyano-2-methyltetrahydroisoquinoline (XIV, p. 1742).

This compound separates on the addition of potassium cyanide to an aqueous solution of 2-methyl-3:4-dihydroisoquinolinium iodide as an amorphous, white precipitate, which quickly becomes crystalline. After crystallisation from ether, it forms long, flat needles, which melt at $77\text{--}78^{\circ}$ (corr.). This compound is almost insoluble in water, but readily soluble in alcohol or ether:

0.1500 gave 0.4197 CO_2 and 0.0942 H_2O . C=76.3; H=7.0.

$\text{C}_{11}\text{H}_{12}\text{N}_2$ requires C=76.7; H=7.0 per cent.

Bis-(2- β -methylaminoethylbenzylidene)acetone (XI or XII, p. 1741).

This base separates as a colourless oil on the addition of acetone and aqueous sodium hydroxide to an aqueous solution of 2-methyl-3:4-dihydroisoquinolinium chloride. It becomes crystalline on keeping, and, after recrystallisation from dry ether, forms colourless, silky needles, which melt at $105\text{--}106^{\circ}$ (corr.), and are anhydrous. This base is insoluble in water, easily soluble in alcohol, and moderately easily so in ether:

0.1440 gave 0.4178 CO_2 and 0.1089 H_2O . C=79.1; H=8.5.

$\text{C}_{23}\text{H}_{25}\text{ON}_2$ requires C=79.2; H=8.1 per cent.

The *dihydriodide* separates in clusters of white, feathery needles on neutralising an acetone solution of the base with hydriodic acid.

This salt decomposes, and becomes orange at about 180° (corr.). It is anhydrous, and is very sparingly soluble in water or alcohol:

0.1571 gave 0.2619 CO_2 and 0.0724 H_2O . $\text{C}=45.5$; $\text{H}=5.2$.

$\text{C}_{23}\text{H}_{25}\text{ON}_2, 2\text{HI}$ requires $\text{C}=45.7$; $\text{H}=5.0$ per cent.

Oxidation of 1-Benzylhydrocotarnine.

Ten grams of 1-benzylhydrocotarnine, 20 grams of sulphuric acid, and 150 c.c. of water were heated for half an hour on the water-bath with 7 grams of pyrolusite, containing 80 per cent. of manganese dioxide; the reaction product was worked up in the usual manner, and gave 2.7 grams of cotarnine, that is, 35 per cent. of the theoretical.

Oxidation of 1-Propylhydrocotarnine.

Seven grams of 1-propylhydrocotarnine, 20 grams of sulphuric acid, and 150 c.c. of water were heated for one hour on the water-bath with 5.8 grams of pyrolusite, containing 80 per cent. of manganese dioxide. The product was extracted with ether, which removed 0.1 gram of brown, resinous matter, and mixed with solid potassium iodide, which caused the precipitation of 4.5 grams of crude 1-propylhydrocotarnine hydriodide; this was removed by filtration, and the liquor rendered alkaline by sodium carbonate, when a quantity of resinous matter separated, together with the manganese carbonate. After filtration, the liquor was extracted with ether, which removed 0.25 gram of a brown oil, from which a further small quantity of crystalline 1-propylhydrocotarnine hydriodide was obtained. The final mother liquor was mixed with aqueous sodium hydroxide and again extracted with ether, which removed only 0.25 gram of a brown gum, from which no crystalline material could be obtained.

It is, therefore, clear that under these conditions a large proportion of the 1-propylhydrocotarnine escapes oxidation, and that no cotarnine is formed.

Oxidation of 1-Ethylhydrocotarnine.

Seventeen grams of 1-ethylhydrocotarnine were heated for three-quarters of an hour on the water-bath with 50 grams of sulphuric acid, 400 c.c. of water, and 15 grams of pyrolusite, containing 80 per cent. of manganese dioxide; more than 10 grams of unchanged 1-ethylhydrocotarnine were recovered from the product of the reaction, but no cotarnine was obtained.

Oxidation of Tetrahydropapaverine.

Thirty grams of tetrahydropapaverine were oxidised with 60 grams of sulphuric acid, 500 c.c. of water, and 20 grams of pyrolusite, containing 80 per cent. of manganese dioxide. The product was worked up in the same way as that from *N*-benzoyltetrahydropapaverine, and gave 13 grams of a brown liquid base, liberated by sodium carbonate. On dissolving this in acetone and neutralising with hydrochloric acid, 8 grams of 6:7-dimethoxy-3:4-dihydroisoquinoline hydrochloride were obtained.

Oxidation of 1:2-Dihydropapaverine.

Eight grams of 1:2-dihydropapaverine, 16 grams of sulphuric acid, 120 c.c. of water, and 5 grams of pyrolusite were heated for three-quarters of an hour on the water-bath; the liquor deposited, on cooling, a quantity of crystalline 1:2-dihydropapaverine hydrogen sulphate, which yielded 5.6 grams of 1:2-dihydropapaverine. On working up the mother liquor in the usual manner, further small quantities of the same base were obtained, but no crystalline degradation product could be isolated.

THE WELLCOME CHEMICAL WORKS,
DARTFORD, KENT.

CXCII.—*A Method of Harmonising the Atomic Weights.*

By JAMES MOIR, D.Sc., M.A.

THE idea now to be presented occurred to the author eighteen months ago, but as it gave an incorrect result when applied to carbon as 12.00 ($O = 16$), it was not pursued farther. The recent determinations, however, of Dr. A. Scott give a value in agreement with the theory, and the author ventures therefore to put it forward in a new form as modified by the appearance of A. Egerton's paper (this vol., 238).

Briefly, the author assumes the cause of valency, at all events the fundamental valency of each element, to be the presence, in varying numbers, of a sub-element of atomic weight $\frac{1}{112}$ (probably eight or nine electrons *), practically in the same way as Sir W. Ramsay assumes the electron to behave. If this be denoted by μ , then the univalent elements contain 1μ , the bivalent 2μ , the trivalent 3μ , and so on. In addition, the author conceives the main bulk of the mass of the elements to be due to polymerisation of an entity consisting of the hydrogen atom less the aggregation μ . Denoting this by \bar{H} , we have

* Fifteen, according to the recent redetermination of the electron as 0.00060.

for example: $H = \bar{H} + \mu$; $Li = 7\bar{H} + \mu$; $C = 12\bar{H} + 4\mu$; $O = 16\bar{H} + 2\mu$; $Ne = 20\bar{H}$; $Na = 23\bar{H} + \mu$; $Ag = 108\bar{H} + \mu$; $Cs = 133\bar{H} + \mu$. The elements which do not agree with this system are probably not direct polymerides of \bar{H} ; but their atomic weights can practically all be expressed in the above way, by having recourse to a fraction of one decimal place exactly. This assumes the existence of another sub-element of exactly one-tenth the weight of hydrogen. Thus, for example: $Gl = 9\cdot1\bar{H} + 2\mu$; $Mg = 24\cdot3\bar{H} + 2\mu$; $Si = 28\cdot3\bar{H} + 4\mu$; $Cr = 52\cdot1\bar{H} + 6\mu$; $Cl = 35\cdot5\bar{H} + \mu$; $Ba = 137\cdot5\bar{H} + 2\mu$, and so on. Although this system savours of manipulation, it will be found that the results calculated by it agree in a most remarkable way with the experimental values.

It should be noted by the way that most of the agreement found by Egerton in his calculations is due to mathematical necessity, for when a number, say N , is divided by $1\cdot0078$, the true result is $N(1 - 0\cdot0078 + 0\cdot00006)$, that is, the error in assuming it to be $N - 0\cdot0078N$ does not affect the third place of decimals unless N is large. The values in column V ($H=1$) on p. 239 of his paper have been calculated from $N/1\cdot0078$, except, curiously enough, in the case of oxygen, where $N(1 - 0\cdot0078)$ has been used; this value should therefore (to be consistent) be $15\cdot8763$.

The following table exhibits the author's results; and column IV,

TABLE

I.	II.	III.	IV.	V.
Symbol.	Natural formula (\bar{H} taken equal to 1).	Formula $\times 112$.	Calculated atomic weight $O = 16\cdot000$	Error.
H.....	1 + μ	113	1\cdot0078	nil
He	4	448	3\cdot9955	?
Li	7 + μ	785	7\cdot0011	?
Gl	9\cdot1 + 2 μ	1021	9\cdot106	?
B.....	11 + 3 μ	1235	11\cdot014	0\cdot01
C.....	12 + 4 μ	1348	12\cdot022	nil
N.....	14 + 3 μ	1571	14\cdot011	?
O.....	16 + 2 μ	1794	16\cdot000	nil
F.....	19 + μ	2129	18\cdot988	0\cdot01
Ne	20	2240	19\cdot978	0\cdot02
Na	23 + μ	2577	22\cdot984	0\cdot016
Mg	24\cdot3 + 2 μ	2724	24\cdot295	0\cdot025
Al	27\cdot1 + 3 μ	3038	27\cdot095	?
Si	28\cdot3 + 4 μ	3174	28\cdot308	?
P.....	31 + 3 μ	3475	30\cdot993	?
S.....	32\cdot1 + 2 μ	3597	32\cdot080	0\cdot01
Cl	35\cdot5 + μ	3977	35\cdot4695	?
A.....	40	4480	39\cdot957	0\cdot04
K.....	39\cdot1 + μ	4380	39\cdot064	0\cdot03
Ca	40\cdot1 + 2 μ	4493	40\cdot072	0\cdot02

TABLE (continued).

I.	II.	III.	IV.	V.
Symbol.	Natural formula (\bar{H} taken equal to 1).	Formula $\times 112$.	Calculated atomic weight $O = 16\cdot000$	Error.
Sc	44·7 + 3 μ	4942	44·08	0·02
Ti	48·1 + 4 μ	5391	48·08	0·02
V	51·2 + 5 μ	5739	51·19	?
Cr	52·1 + 6 μ	5841	52·094	?
Mn	55 + 2 μ	6162	54·956	0·026
Fe	55·9 + 2 μ	6263	55·858	nil
Ni	58·7 + 2 μ	6576	58·65	0 03
Co	59 + 2 μ	6610	58·95	?
Cu	63·6 + 2 μ	7125	63·546	0·02
Zn	65·4 + 2 μ	7327	65·347	0·02
Ga	70 + 3 μ	7843	69·95	?
Ge	72·5 + 4 μ	8124	72·46	?
As	75 + 2 μ	8403	74·95	?
Se	79·3 + 2 μ	8884	79·23	?
Br	80 + μ	8961	79·920	nil
Kr	83	9296	82·91	?
Rb	85·5 + μ	9577	85·415	0·035
Sr	87·7 + 2 μ	9824	87·617	nil
Y	89 + 3 μ	9971	88·93	0·07 ?
Zr	90·6 + 4 μ	10151	90·53	0·07 ?
Cb	93·6 + 5 μ	10488	93·54	0·04
Mo	96 + 6 μ	10758	95·95	0·05
Ru	101·8 + 8 μ	11410	101·76	?
Rh	103 + 8 μ	11544	102·96	?
Pd	106·8 + 2 μ	11964	106·70	nil
Ag	108 + μ	12097	107·889	nil
Cd	112·5 + 2 μ	12602	112·40	nil
In	115 + 3 μ	12883	114·90	?
Sn	119 + 4 μ	13332	118·905	0·095
Sb	120·3 + 3 μ	13477	120·20	nil
Te	127·6 + 2 μ	14293	127·48	?
I	127 + μ	14225	126·87	0·05
X	130	14560	129·86	?
G	133 + μ	14897	132·86	?
Ba	137·5 + 2 μ	15402	137·366	nil
La	139 + 3 μ	15571	138·87	0·13 ?
Ce	140·3 + 3 μ	15717	140·175	0·07
Pr	140·7 + 3 μ	15762	140·58	?
Nd	144·5 + 3 μ	16187	144·37	?
Sa	150·5 + 3 μ	16859	150·36	?
Eu	152 + 3 μ	17027	151·86	?
Yb	172 + 3 μ	19267	171·84	?
Ta	181 + 5 μ	20277	180·845	0·15
W	184 + 6 μ	20614	183·850	0·15
Os	191 + 8 μ	21400	190·86	?
Ir	193·3 + 8 μ	21658	193·16	?
Pt	195·2 + 4 μ	21866	195·01	nil
Au	197·4 + 3 μ	22112	197·21	nil
Hg	200·2 + 2 μ	22424	200·00	nil
Tl	204·2 + μ	22871	203·99	nil
Pb	207·3 + 2 μ	23220	207·10	nil
Bi	208·3 + 3 μ	23333	208·11	nil
Ra	226 + 2 μ	25314	225·77	?
Th	233 + 4 μ	26100	232·78	0·3
U	239 + 6 μ	26774	238·80	0·3

wherein the atomic weights are reduced to $O = 16$ from column II where $O = 16.018$, shows a very close approximation to the accepted atomic weights.

The system therefore does not break down, as does Egerton's, in the case of any of the well-ascertained atomic weights; and the author hopes that it will evoke interest, even if only as a curiosity of coincidences.

MINES DEPARTMENT,
JOHANNESBURG.

CXCIII. — *The Constitution of Polynitrophenols in Alkaline Solution.*

By BERTRAM HAWARD BUTTLE and JOHN THEODORE HEWITT.

THE suggestion thrown out years ago by Armstrong that the colour of the salts of the nitrophenols can be best explained by assigning to them a quinonoid constitution has received considerable support during the past few years, and probably the number of chemists who disagree with the view that ortho- and para-nitrophenols and their metallic salts have radically different constitutions is very limited, the markedly different absorption spectra of these compounds in neutral (or acid) and alkaline solutions (Baly, Edwards, and Stewart, *Trans.*, 1906, **89**, 519, 521), and the isolation of *aci*-esters by Hantzsch and Gorke (*Ber.*, 1906, **39**, 1073; compare Kauffmann, *Ber.*, 1907, **40**, 843, 4547, and Hantzsch, *ibid.*, 1906, **39**, 1959, and 1907, **40**, 1556), being scarcely capable of any other interpretation.

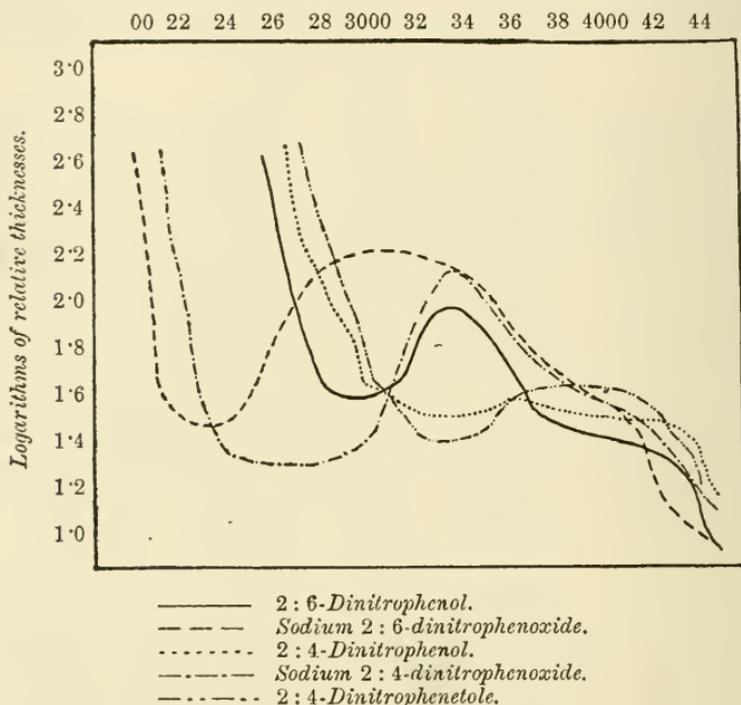
To the authors of the present communication the question of the absorption spectra of these compounds has been of considerable interest as giving an example of the dependence of oscillation frequency on the length of chain of conjugate linkings, and, further, that one has a chance of deciding, at any rate in particular instances, whether, when salt formation is accompanied by quinonoid rearrangement, and the latter may be either of ortho- or of para-type, which of the two possible configurations is preferred.

Respecting the first of these questions, the curves of Baly, Edwards, and Stewart (*loc. cit.*) seem to give a very decided answer, for the oscillation frequency of the para-compound is greater than that of the ortho-isomeride, even in neutral solution, whilst, on comparing the alkaline solutions, one sees immediately that, whereas the head of the band in the case of sodium *p*-nitro-

phenoxide corresponds with an oscillation frequency of about 2450, that of the corresponding ortho-salt is about 2300. Inspection of the quinonoid formulæ of the isomeric sodium salts shows that whilst both possess an equal number of double linkings, a longer conjugate chain exists in the case of the ortho- than of the para-compound. It will be noted that our results for polynitrophenols fully correspond.

The second point, preference for ortho- or para-quinonoid configuration, is of some interest from several points of view. Thus,

FIG. 1.

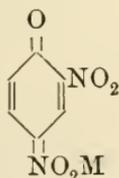
Oscillation frequencies.

many compounds, which until a few years ago were generally regarded as possessing para-quinonoid structure, have been formulated by Kehrmann with an ortho-quinonoid constitution (*Ber.*, 1899, **32**, 927; 1905, **38**, 2577; 1907, **40**, 1960, and many other papers), despite the excellent arguments adduced by Hantzsch to the contrary, and evidence which has been obtained from the examination of acridine derivatives (Hewitt and Fox, *Trans.*, 1904, **85**, 529; 1905, **87**, 1058). The study of the absorption spectra of neutral and alkaline solutions of 2:4-dinitrophenol seemed likely to give a

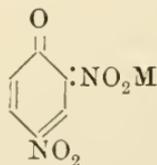
due to the relative probability of which structure would be produced when both were possible.

As will be seen by reference to Fig. 1, the head of the band in the case of an alkaline solution of 2:6-dinitrophenol is near to oscillation frequency 2300, very near, in fact, to the position found by Baly and his co-workers for *o*-nitrophenol in alkaline solution, and although the head of the band is broader in the case of the dinitrophenol, a comparison of the two frequency curves shows their great similarity. The general resemblance holds when one compares the curves for a neutral solution of *o*-nitrophenol with that of the 2:6-dinitrophenol to which dilute hydrochloric acid has been added.

A marked difference exists, however, between the absorption spectra of the alkaline solutions of 2:4- and 2:6-dinitrophenols. An acid solution of the 2:4-dinitrophenol shows a broad band with head at an oscillation frequency of nearly 3400, and comparison with 2:4-dinitrophenetole exhibits sufficient similarity to lead to the conclusion that the free compound exists in acid solution as a true dinitrophenol. The alkaline solution of the 2:4-dinitrophenol has an absorption spectrum which, although differing markedly from that of the alkaline *p*-nitrophenol, nevertheless resembles this to a greater degree than the alkaline solution of the *o*-nitrophenol. Thus, whilst *o*-nitrophenol and 2:6-dinitrophenol in alkaline solutions both give absorption bands having heads at an oscillation frequency of about 2300, the head of the corresponding band in the case of alkaline *p*-nitrophenol is at 2450, whilst with 2:4-dinitrophenol the band is much broader and less persistent, the head corresponding to an oscillation frequency of somewhere about 2700. Thus, of the two possible quinonoid structures for alkali salts of 2:4-dinitrophenol,



(I.)



(II.)

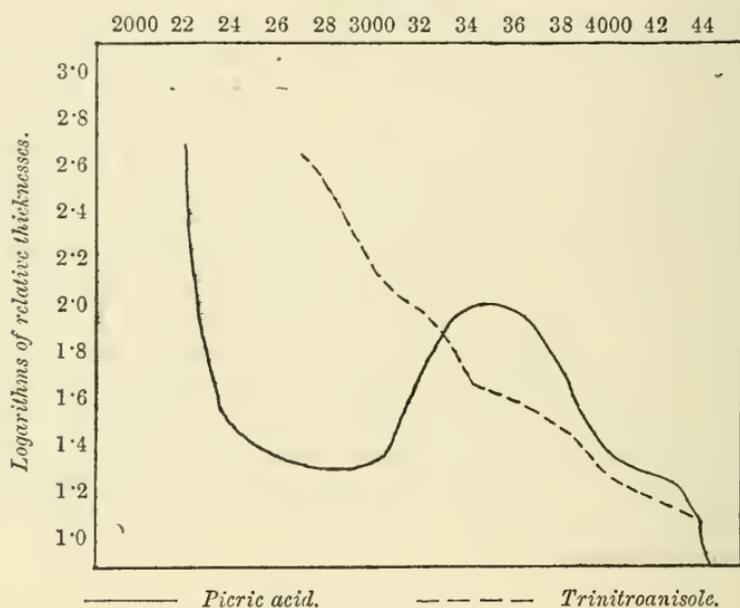
the *para*-quinonoid (I) is to be preferred.

The specimens of 2:4- and 2:6-dinitrophenols employed in this work were obtained from Schuchardt, recrystallised and checked as to purity by means of their melting points. The 2:4-dinitrophenetole was a specimen prepared some years ago in a high state of purity by one of us; for this work it was again recrystallised, and showed a melting point of 86°. The aqueous alkaline solutions, as spectroscopically examined, were *N*/10,000 with regard to the

dinitrophenol, the alkali, which was present in ten times the equivalent amount, being $N/1000$. The acid solutions contained 100 molecules of hydrochloric acid per molecule of dinitrophenol. The object of this considerable excess of hydrochloric acid was, of course, to prevent ionisation, since the ions would doubtless be produced from the *aci*-forms of the phenolic compounds. Bader determined the dissociation constants of several substituted phenols in 1890 (*Zeitsch. physikal. Chem.*, **6**, 289), and obtained values of K for 2:4- and 2:6-dinitrophenols of 0.0080 and 0.0174 respec-

FIG. 2.

Oscillation frequencies.



tively; it is evident, therefore, that under the conditions employed ionisation of the free dinitrophenols may be disregarded.

For purposes of comparison, acid and alkaline solutions of picric acid were also examined, the molecular proportions of trinitrophenol, alkali, and acid being the same as in the preceding cases. In these circumstances, practically no difference was found in the absorption spectra, a result which might be expected, considering the strength of picric acid and its almost complete dissociation at even quite moderate dilutions. The curve reproduced (continuous line, Fig. 2) is that obtained from measurements of an acid solution. If one could obtain a solution of the true trinitrophenol (in a

solvent transparent to the ultraviolet rays), it would doubtless give an entirely different absorption spectrum, judging from the results obtained with an alcoholic solution of trinitroanisole,* and the fact that solutions of picric acid vary in colour according to the ionising power of the solvent. Thus Walden (*Ber.*, 1899, **32**, 2864) describes the solution in liquid sulphur dioxide as being colourless, although those of phenol and quinol are distinctly yellow. Marckwald (*Ber.*, 1900, **33**, 1128) also draws attention to the fact that ordinary yellow picric acid gives with light petroleum a colourless solution, which, however, immediately communicates a yellow colour to water when shaken with it.

The close similarity between the absorptions exhibited by alkaline solutions of 2:4-dinitrophenol and of picric acid (head about 2800) point to the ions of both these substances having similar structures when they are to be considered as nitro-derivatives of *aci-p*-nitrophenol; that is, having para- rather than ortho-quinonoid structure.

The strengths of the nitrated nitrophenols as acids is of some interest in connexion with the identification of the salts of 2:4-dinitrophenol and of picric acid as *p*-quinonoid compounds. The dissociation constants, as found by Bader (*loc. cit.*) for *o*- and *p*-nitrophenols and their higher nitrated derivatives, are as follows.

Derivatives of <i>o</i> -Nitrophenol.		Derivatives of <i>p</i> -Nitrophenol.	
2-Nitrophenol	0·000043	4-Nitrophenol	0·000012
2:3-Dinitrophenol	0·0012	2:4-Dinitrophenol	0·0080
2:5-Dinitrophenol	0·0007	3:4-Dinitrophenol	0·0004
2:6-Dinitrophenol	0·0174	2:4:6-Trinitrophenol.....	Strong acid.

In each case it will be noted that a nitrophenol is strengthened as an acid by the introduction of another nitro-group, the effect produced being greatest when the second nitro-group enters the meta-position with respect to the nitro-group already present.

There is possibly some connexion between this influence and the weakening of the attachment of nitro-groups to aromatic nuclei produced by the presence of other nitro-groups in a meta-position. On this mobility depends the oxazine synthesis of Turpin (*Trans.*, 1891, **59**, 722), the production of dinitroanisole from 1:3:5-trinitrobenzene (Lobry de Bruyn, *Rec. trav. chim.*, 1890, **9**, 209), and several azine syntheses (see Kehrmann, *Ber.*, 1899, **32**, 2601), whilst it is noticeable that the trinitroacetylaminophenol described by Meldola (*Trans.*, 1906, **89**, 1935) and subsequently employed by Meldola and Hay in many syntheses (*Trans.*, 1908, **93**, 1659; 1909, **95**, 1033) has one of its nitro-groups easily removable, the

* Prepared from anisole by extreme nitration, and crystallised from alcohol; m. p. 68°. Found N=17·5; $C_7H_5O_7N_3$ requires N=17·3 per cent.

other two nitro-groups being oriented ortho- and meta- to the group so readily eliminated as nitrous acid.

In conclusion, we wish to express our indebtedness to the Government Grant Committee for a grant by which the greater part of the expense of this investigation has been defrayed.

EAST LONDON COLLEGE.

CXCIV.—*The Solubility of Bismuth Trisulphide in Alkali Sulphides and of Bismuth Trioxide in Alkali Hydroxides.*

By JOSEPH KNOX (Carnegie Research Fellow of Aberdeen University).

STILLMAN (*J. Amer. Chem. Soc.*, 1896, **18**, 683) states that bismuth sulphide is soluble to a considerable extent in sodium sulphide, whilst Stone (*ibid.*, 1091), who confirmed this result, found that if the bismuth was first precipitated as sulphide from an acid solution, and then treated with alkali sulphide, little, if any, dissolved. Stillman precipitated a solution of bismuth nitrate with excess of sodium sulphide, warmed to a temperature near the boiling point for twenty minutes, filtered, and determined the bismuth in the filtrate. He gives, however, only one quantitative experiment, in which, moreover, the strength of the sodium sulphide employed is uncertain. Stone precipitated bismuth sulphide from a dilute acid solution of the chloride, filtered, and heated the precipitate with a large excess of potassium sulphide or of ammonium sulphide for half an hour. The undissolved sulphide was collected, redissolved, and the bismuth determined as the oxide. In both cases the bismuth trioxide found agreed with the amount of bismuth originally taken as chloride. Stone therefore concluded that bismuth sulphide, precipitated from acid solution, is not dissolved by subsequent treatment with alkali sulphides.

Neither author gives the method of preparation or the composition of the alkali sulphides employed. Since the term, "alkali sulphide solution," is applied in analytical chemistry to the solutions obtained by saturating the hydroxides with hydrogen sulphide to a greater or less extent, that is, to solutions of the alkali hydro-sulphides or of the hydrosulphides and hydroxides in varying proportions, it is possible that such solutions were used by Stone,

instead of those containing the dissolved substance in the stoichiometric proportions represented by the formulæ Na_2S , K_2S , etc. This would explain the discrepancy between the results of Stone and those of the present investigation.

So far as the author is aware, no further work has been done on the solubility of bismuth sulphide in alkali sulphides. Owing to the important bearing of the subject on analytical chemistry, and to its interest from the theoretical point of view, the present investigation was undertaken in order to ascertain the nature of the reaction between bismuth sulphide and alkali sulphides, and the relation between solubility and concentration.

From the position of bismuth in the periodic system as the highest member of the fifth group, it might be expected that bismuth sulphide would, like the corresponding arsenic and antimony compounds, form complex anions with the sulphur ions of alkali sulphide solutions, although to a much smaller extent, on account of its greater electro-affinity compared with these elements (Abegg and Bodländer, *Zeitsch. anorg. Chem.*, 1899, **20**, 453; Abegg, *ibid.*, 1904, **39**, 330). Further, it is almost certain that the behaviour of bismuth sulphide towards solutions of sodium and potassium sulphides will be practically the same, owing to the similarity in constitution of the two solutions.

The bismuth sulphide used in the following solubility determinations was mainly "Kahlbaum's precipitated," which was freed from admixed sulphur by extraction with carbon disulphide and dried at 100—110°. It contained traces of oxychloride, which, however, in presence of the large excess of alkali sulphide used, have probably no effect on the solubility determination. In several experiments the bismuth sulphide used was prepared by precipitating a dilute solution of bismuth chloride, acidified with hydrochloric acid, with hydrogen sulphide, washing the precipitate, and drying at 100—110°. The sulphide so prepared gave the same solubility as Kahlbaum's. The sodium sulphide solutions were prepared by saturating a measured volume of standard sodium hydroxide, free from carbonate, with hydrogen sulphide in a graduated flask, expelling the excess of hydrogen sulphide by a current of hydrogen, adding a volume of sodium hydroxide equal to that originally used, and diluting to the mark with air-free distilled water. The potassium sulphide solutions were prepared similarly. The solubility in each strength of alkali sulphide was determined several times, and the alkali sulphide used in each determination was freshly prepared. This procedure eliminates, as far as possible, any error due to slight divergences in the composition of the solution from the theoretical, caused by the

impossibility of stopping the hydrogen current used to expel the excess of hydrogen sulphide at the exact point. These divergences will, however, always be small, since the concentration of undissociated hydrogen sulphide in alkali sulphide solutions, and hence the partial pressure of hydrogen sulphide over them is exceedingly minute (Knox, *Trans. Faraday Soc.*, 1908, **4**, 29). All operations were performed, as far as possible, in an atmosphere of hydrogen, so as to avoid oxidation of the solutions by atmospheric oxygen.

The solubility determinations were carried out as follows. The bismuth sulphide was shaken with the alkali sulphide solutions in a thermostat at 25° for about three days. In most cases experiments were also carried out in which the shaking was continued for a much longer period, in order to ensure that the equilibrium had been attained. In most cases, too, the equilibrium was attained from both sides. On the one hand, the sulphide solutions were shaken at 25° with bismuth sulphide until saturation occurred, and, on the other, the sulphide solutions were first saturated with bismuth sulphide at about 80°, and then shaken in the thermostat at 25° until equilibrium for this temperature was reached. The equilibrium attained under these different conditions was always the same. For the analyses, the bottles were hung in the thermostat until the solid had completely settled; 100 c.c. of the clear solution were then transferred to a beaker and carefully acidified with a slight excess of hydrochloric acid. This precipitated most of the bismuth sulphide, although the supernatant liquid remained brown, apparently owing to some of the sulphide remaining in colloidal solution, since the liquid cleared on standing. Hydrogen sulphide was passed in to complete the precipitation, and the precipitate was collected in a Gooch's crucible, washed with aqueous hydrogen sulphide, then with alcohol, and finally with carbon disulphide, and dried at 100—105°.

As will be seen from the tables, the agreement between the different determinations for a given concentration is not so good as is usual in a solubility determination, but this is probably accounted for by slight differences in the composition of the solutions, by differences in the size of the grains of the bismuth sulphide (Ostwald, *Zeitsch. physikal. Chem.*, 1900, **34**, 495), and by slight oxidation of the solutions.

The following table gives the solubility of dried precipitated

Concentration of sodium sulphide, mole/litre.	Number of determinations.	Bismuth sulphide dissolved: gram per 100 c.c. of solution, mean result.
0.5	5	0.0040 ± 0.0005
1.0	5	0.0238 ± 0.0016
1.5	3	0.1023 ± 0.0025

bismuth sulphide in sodium sulphide solutions. The solutions are greenish-yellow in colour.

In potassium sulphide solutions, the solubility for the same concentration is rather greater:

Concentration of potassium sulphide, mole/litre.	Number of determinations.	Bismuth sulphide dissolved : gram per 100 c.c. of solution, mean result.
0.5	4	0.0042 ± 0.0003
1.0	4	0.0337 ± 0.0017
1.25	5	0.0639 ± 0.0016

Since both freshly precipitated moist bismuth sulphide and dried precipitated bismuth sulphide dissolve in potassium sulphide solutions, it is difficult to explain the results obtained by Stone except on the assumption that he used potassium hydrosulphide instead of potassium sulphide solutions.

In the case of both sodium and potassium sulphides, the solubility increases rapidly with the concentration of the alkali sulphide, and is approximately proportional to the cube of the concentration.

The addition of alkali hydroxide to the alkali sulphide increases the solubility greatly. The following tables show the effect of sodium hydroxide and of potassium hydroxide on the solubility:

Solubility of Bismuth Sulphide in Sodium Sulphide with the addition of Sodium Hydroxide.

Concentration of sodium sulphide, mole/litre.	Concentration of sodium hydroxide, mole/litre.	Number of determinations.	Bismuth trisulphide dissolved : gram per 100 c.c. of solution, mean result.
0.5	1.0	7	0.0185 ± 0.0020
1.0	1.0	4	0.0838 ± 0.0022

Solubility of Bismuth Sulphide in Potassium Sulphide with the addition of Potassium Hydroxide.

Concentration of potassium sulphide, mole/litre.	Concentration of potassium hydroxide, mole/litre.	Number of determinations.	Bismuth sulphide dissolved : gram per 100 c.c. of solution, mean result.
0.5	1.0	4	0.0240 ± 0.0010
1.0	1.0	2	0.1230 ± 0.0014
1.25	1.25	1	0.2354

The solvent action of alkali hydrosulphides and hydroxides on precipitated bismuth sulphide was next investigated, since there was a possibility, judging from analogy to arsenic and antimony sulphides, that it might dissolve to a slight extent.

The hydrosulphide solutions were prepared by saturating the hydroxides with hydrogen sulphide, and expelling the excess of this gas by a current of hydrogen. Dried precipitated bismuth sulphide

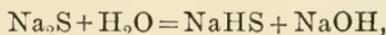
was shaken with *N*- and 2*N*-sodium hydrosulphide and potassium hydrosulphide solutions for periods varying from twelve to twenty days. The solid was allowed to settle completely, and the clear, colourless, supernatant liquid withdrawn, faintly acidified with hydrochloric acid, and saturated with hydrogen sulphide. No trace of a precipitate or even of a brown coloration was obtained. On adding sodium hydroxide to the remaining sodium hydrosulphide solution, and again shaking for a few minutes, the solution assumed the greenish-yellow colour characteristic of solutions of bismuth sulphide in alkali sulphides. Bismuth sulphide is, therefore, insoluble in alkali hydrosulphides. This is also proved by the action of hydrogen sulphide on solutions of bismuth sulphide in alkali sulphides. On saturating such a solution with hydrogen sulphide, the bismuth sulphide is completely precipitated.

For the solubility experiments in alkali hydroxides, it was necessary that the bismuth sulphide used should contain traces neither of the oxide, which is slightly soluble in alkali hydroxides (see below), nor of the oxychloride, which reacts with alkali hydroxides to a certain extent giving the hydroxide BiO_2H (Herz and Muhs, *Zeitsch. anorg. Chem.*, 1904, **39**, 115). The first solubility determinations, made with dried precipitated bismuth sulphide, gave a solubility of the same order as that of bismuth oxide in alkali hydroxides. This was subsequently found to be due to slight oxidation of the sulphide during the drying, or to the presence of traces of oxychloride. It was found very difficult to prepare bismuth sulphide free from oxychloride by precipitation from a hydrochloric acid solution. Prolonged washing with aqueous hydrogen sulphide is necessary to remove the last traces of oxychloride. In order to avoid these sources of error, freshly precipitated, moist bismuth sulphide, which had been repeatedly washed with aqueous hydrogen sulphide and finally with air-free distilled water, was shaken with *N*- and 2*N*-sodium hydroxide for fifteen and thirteen days respectively. On acidifying the clear solution with hydrochloric acid and saturating with hydrogen sulphide, no trace of a precipitate or brown coloration was obtained. Bismuth sulphide is therefore insoluble in alkali hydroxides.

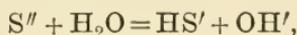
That the solutions of bismuth sulphide in alkali sulphides are not colloidal is proved by the following considerations. The same equilibrium is attained from both sides, and independently of the time of shaking. The solutions are quite stable; after months they still retain bismuth and their characteristic greenish-yellow colour, although they contain large quantities of electrolytes, which, as a rule, act as more or less rapid precipitants for colloids. The bismuth is not removed by filtering the solution through a very finely porous

cell. The fact that the solutions are prepared from dried precipitated bismuth sulphide is also against the probability of their being colloidal. Finally, the properties of the solutions do not agree with those of colloidal solutions of bismuth sulphide (Abegg's *Handbuch der anorg. Chem.*, III, 3, 662).

Since bismuth sulphide is insoluble both in alkali hydrosulphides and hydroxides, that is, does not form a complex anion with either SH' or OH', its solubility in alkali sulphide solutions must be due to the formation of a complex anion with the sulphur ion, S'', of these solutions. This view explains the increase in the ratio, bismuth sulphide dissolved/concentration of alkali sulphide, with increasing concentration of the alkali sulphide, and also the effect of the addition of alkali hydroxide in increasing the solubility of bismuth sulphide. The explanation is as follows. Sodium sulphide in aqueous solution is hydrolysed to a very large extent into sodium hydrosulphide and hydroxide (Küster and Heberlein, *Zeitsch. anorg. Chem.*, 1905, 43, 53; Knox, *loc. cit.*) according to the equation:



or, writing the ionic equation:



and, since it is the salt of a weak acid and a strong base, the hydrolysis must increase with dilution. The relative concentration of the S''-ions must, therefore, diminish with dilution, and, since the solubility of bismuth sulphide depends on the S''-ion concentration, the ratio of bismuth sulphide dissolved to sodium sulphide will also diminish with dilution. From the hydrolysis equation, it is also evident that the addition of alkali hydroxide, by increasing the concentration of OH'-ions, will diminish the degree of hydrolysis, thus increasing the concentration of the S''-ion, and hence the solubility of bismuth sulphide in the alkali sulphide. The same considerations apply also in the case of potassium sulphide. The existence of the solid compounds KBiS₂, NaBiS₂ (Schneider, *Pogg. Ann.*, 1869, 136, 460; Milbauer, *Zeitsch. anorg. Chem.*, 1905, 42, 433), and Bi₂S₃.4K₂S.4H₂O (Ditte, *Compt. rend.*, 1895, 120, 186) also confirms the view that the solubility is due to complex formation with the S''-ion.

Bismuth sulphide, therefore, forms, like the corresponding arsenic and antimony compounds, complex anions with the S''-ion, but not to an appreciable extent with SH'- or OH'-ions. From the solubility determinations alone, however, it is not possible to arrive at the formula of the complex.

The importance of this reaction in analytical chemistry has

already been emphasised by Stillman (*loc. cit.*). In the separation of the copper sub-group from the arsenic sub-group by means of alkali sulphides, the quantitative determination of bismuth would be vitiated, and small quantities of bismuth might easily be missed altogether.

The action of sodium disulphide and of ammonium sulphide solutions on bismuth sulphide was also studied, in view of their importance analytically in the separation of the copper and arsenic sub-groups.

The sodium disulphide solutions were prepared by dissolving the requisite quantity of sulphur (crystallised from carbon disulphide) in sodium sulphide solutions. In the solubility determinations, dried precipitated bismuth sulphide was shaken with the sodium disulphide solution until equilibrium was established. A definite volume of the clear solution was then withdrawn, and acidified with hydrochloric acid. The bismuth sulphide was precipitated along with the excess of sulphur. Hydrogen sulphide was passed in until the supernatant liquid became clear, when the precipitate was collected in a Gooch's crucible, washed with aqueous hydrogen sulphide, then with alcohol, and finally with carbon disulphide, dried, and weighed. The washing with carbon disulphide was repeated until the weight was constant. As the mean of four determinations, in which the times of shaking were varied greatly, 100 c.c. of *N*-sodium disulphide solution were found to dissolve 0.0090 ± 0.0010 gram of bismuth sulphide. This is only about a third of the solubility in the corresponding strength of the monosulphide. This result confirms the view that the solubility of bismuth sulphide in alkali sulphides is due to the formation of a complex anion with the S'' -ion, since in polysulphide solutions a large proportion of the S'' -ions are used up in forming the complexes S_2'' , S_3'' , etc., with the dissolved sulphur, and are, therefore, not available for complex-formation with bismuth sulphide. In solutions of the higher polysulphides, the solubility would be still less than in the disulphide.

The ammonium sulphide solution was prepared in the same way as the sodium sulphide, except that the hydrogen sulphide used to saturate the ammonia solution was washed by ammonia of the same strength, and the expulsion of the excess of hydrogen sulphide by a current of hydrogen was omitted. In *2N*-ammonium sulphide, which had been shaken with dried precipitated bismuth sulphide for ten days, no trace of dissolved bismuth sulphide was found. The exceedingly small concentration of S'' -ions in ammonium sulphide solutions (Knox, *loc. cit.*) explains the insolubility of bismuth sulphide.

Solubility of Bismuth Oxide in Sodium Hydroxide Solutions.

The bismuth oxide was prepared either by igniting the basic nitrate to low redness, or by precipitating the basic nitrate from a solution of the normal nitrate by diluting with water, digesting the precipitate on the water-bath repeatedly, first with water and then with sodium hydroxide solutions, washing until free from alkali, drying, and igniting. Both preparations gave the same solubility. The sodium hydroxide solutions used were free from carbonate.

The time of shaking required for the establishment of equilibrium was much longer than in the case of the sulphide solutions. As a rule, two to three weeks were allowed. The solubility determinations were carried out in the same way as for the sulphide. The clear saturated solutions were slightly acidified with hydrochloric acid, and the bismuth precipitated as sulphide. The results are contained in the following table:

Concentration of sodium hydroxide, mole/litre.	Number of determinations.	Bismuth oxide dissolved: gram per 100 c.c. of solution, mean result.
1.0	7	0.0013 ± 0.0002
2.0	6	0.0026 ± 0.0002
3.0	5	0.0049 ± 0.0005

The solutions were colourless, and showed no opalescence.

The solubility is nearly proportional to the concentration of the sodium hydroxide. A few experiments with potassium hydroxide showed that the solubility was much the same as in sodium hydroxide. The same arguments against the colloidal nature of the solutions hold as in the case of the sulphide solutions. Bismuth trioxide, therefore, behaves towards strong bases as the anhydride of a weak acid, but, in agreement with its more electropositive character, to a much less extent than the corresponding oxides of arsenic and antimony.

CHEMICAL DEPARTMENT,
UNIVERSITY OF ABERDEEN.

CXCV.—*The Volumetric Estimation of Mercury and the Estimation of Silver in Presence of Mercury.*

By JOSEPH KNOX (Carnegie Research Fellow of Aberdeen University).

RUPP and Krauss (*Ber.*, 1902, **35**, 2015) describe a volumetric method for the estimation of mercury in a solution of mercuric nitrate by titration with ammonium thiocyanate. The method is the same as Volhard's method for silver, except that the solution must be strongly acid with nitric acid.

The method has been used for some time by the students in this laboratory; the mercuric nitrate solution used by them was made by dissolving a weighed quantity of precipitated mercuric oxide in excess of dilute nitric acid. As the results obtained were consistently rather low, the following investigation was undertaken in order to test the accuracy of Rupp and Krauss' method.

On testing the method by titrating a mercuric nitrate solution, prepared by dissolving precipitated mercuric oxide or red, crystalline mercuric oxide in cold dilute nitric acid, I obtained results for the mercury from 0.4 to 1 per cent. lower than those calculated from the weight of mercuric oxide used. The mercury in the solution was also estimated gravimetrically as sulphide, and the results agreed, within the limits of experimental error, with those calculated from the weight of mercuric oxide dissolved. The mercuric sulphide was collected in a Gooch's crucible, washed with water, alcohol, and then with carbon disulphide until the weight was constant. The explanation of the low results by the volumetric method was found in the fact that the solutions obtained by dissolving mercuric oxide in excess of cold dilute nitric acid invariably contained mercurous nitrate, especially after standing for some time. The effect of small quantities of mercurous salt on the volumetric result is considerable, whereas the gravimetric result is scarcely affected. Thus, for example, 216 grams of mercuric oxide would give 232.07 grams of mercuric sulphide. If the mercuric oxide contained 1 per cent. of mercurous oxide, the gravimetric estimation as sulphide would give 229.74 grams of mercuric sulphide + 2.24 grams of mercurous sulphide = 231.98 grams, compared with 232.07 grams from pure mercuric oxide, a difference of only 0.04 per cent. By the volumetric method 216 grams of mercuric oxide would require 2000 c.c. of *N*-ammonium thiocyanate, whereas if the mercuric oxide contained 1 per cent. of mercurous oxide the amount of thiocyanate required would be 1980 c.c. for the mercuric salt + 10.38

c.c. for the mercurous salt = 1990.38 c.c., compared with 2000 c.c. for pure mercuric oxide, a difference of 0.48 per cent.

As an example of the results actually obtained, the following figures may be given. The first column gives the equivalent normal concentration of the mercuric nitrate solutions calculated from the weight of mercuric oxide used, the second column the concentration calculated from the gravimetric estimation of the mercury as sulphide, and the third column the concentration calculated from the volumetric analysis, on the assumption that all the mercury was in the mercuric form. The ammonium thiocyanate solutions used in the titrations were standardised from a silver nitrate solution, the strength of which was found by estimating the silver gravimetrically as chloride:

	I.	II.	III.
1.....	0.2936	0.2935	0.2914
2.....	0.2972	0.2970	0.2958
3.....	0.1239	0.1238	0.1229

All these solutions gave a turbidity with hydrochloric acid, owing to the precipitation of mercurous chloride.

Pure mercuric nitrate solutions were next prepared by dissolving a weighed quantity of pure distilled mercury in pure concentrated nitric acid. The solution was boiled for a short time and diluted to a definite volume. These solutions contained no mercurous salt even after standing several weeks. The agreement between the results for the strength of the mercuric nitrate solution, as calculated (1) from the weight of mercury dissolved (first column), (2) from the gravimetric estimation as mercuric sulphide (second column), and (3) from the volumetric estimation (third column), is excellent. The volumetric results are calculated from the mean of several closely agreeing titrations:

	I.	II.	III.
1.....	0.1239	0.1240	0.1238
2.....	0.1559	0.1560	0.1559

The method of Rupp and Krauss, therefore, gives perfectly accurate results with pure mercuric nitrate solutions.

Rupp and Krauss further describe a method for determining silver and mercuric mercury together in a solution of their nitrates. The total silver and mercury is determined by titration with standard thiocyanate, whilst the silver is determined in another portion of the solution by titration by Gay-Lussac's method. The determination of the total silver and mercury by thiocyanate is accurate. Thus it was found that 10 c.c. of 0.1559*N*-mercuric nitrate and 25.07 c.c. of 0.09946*N*-silver nitrate

required 37.44 c.c. of 0.1084*N*-ammonium thiocyanate, compared with 37.38 c.c. calculated from the strengths of the silver and mercury solutions.

It has long been known, however, that the determination of silver by Gay-Lussac's method is inaccurate in presence of small quantities of mercury, and impossible in presence of large quantities (see, for example, Fresenius, *Quant. Anal.*, 6th German Ed., Vol. I, p. 309). This effect of mercuric salts is explained by the extremely small extent to which mercuric chloride is dissociated electrolytically (Morse, *Zeitsch. physikal. Chem.*, 1902, **41**, 709; Buttler and Hewitt, *Trans.*, 1908, **93**, 1405). Thus, on adding sodium chloride to a mixture of silver and mercuric nitrates, both of which are dissociated to a large extent in dilute solution, the whole of the Cl^- ions will not be used to precipitate the silver as chloride, but a definite proportion, depending on the solubility product of silver chloride and on the dissociation constant of mercuric chloride, will unite with the Hg^{2+} ions to form undissociated mercuric chloride. It is on this minute degree of electrolytic dissociation of mercuric chloride that the solubility of silver chloride in mercuric nitrate solutions also depends (Morse; Buttler and Hewitt). Yet Rupp and Krauss state that 10 c.c. of *N*/10-silver nitrate and 10 c.c. of 0.2347*N*-mercuric nitrate required 10.01 c.c. of *N*/10-sodium chloride. I have repeated many times the titration of silver with sodium chloride by Gay-Lussac's method in presence of varying quantities of mercuric nitrate, and found that the precipitation of the silver was not complete until 98—99 per cent. of the mercuric nitrate had been converted into undissociated mercuric chloride. Thus, for example, 10 c.c. of 0.09931*N*-silver nitrate and 10 c.c. of 0.2935*N*-mercuric nitrate required, in three different experiments, 28.83, 28.90, and 28.81 c.c. of 0.1342*N*-sodium chloride, and 10 c.c. of 0.09931*N*-silver nitrate and 5.05 c.c. of 0.2935*N*-mercuric nitrate required 18.30 c.c. of 0.1342*N*-sodium chloride. To convert both the silver and the mercuric salt completely into chlorides would have required, in the first case, 29.27 c.c., and in the second case, 18.44 c.c., of the sodium chloride solution, whilst the silver salt alone should have required only 7.40 c.c. in each case. In presence of the mercuric salt, the precipitated silver chloride settles extremely slowly, so that a titration occupies several days. For the estimation of the total silver and mercury in a solution of the nitrates, the method of Rupp and Krauss is, therefore, rapid and accurate. It is, however, useless for the estimation of the metals separately.

For the volumetric estimation of silver in a solution containing silver and mercuric nitrates, a method depending on the solubility

of silver chloride in potassium cyanide was used. The following description of an experiment illustrates the method. Ten c.c. of 0.09979-N-silver nitrate and 10 c.c. of 0.2935N-mercuric nitrate were mixed, and the silver was precipitated completely as chloride by dilute hydrochloric acid. Sufficient hydrochloric acid was added to convert both silver and mercury into chlorides. The silver chloride was coagulated by heating on the water-bath with constant stirring, cooled, and collected on a hardened filter paper. The precipitate was washed with dilute nitric acid, and then with water, until free from chlorides, then paper and precipitate were transferred to a beaker, 25.07 c.c. of 0.0953N-potassium cyanide were added, and the silver chloride dissolved completely. The excess of potassium cyanide was then titrated with 0.09979N-silver nitrate until a permanent turbidity appeared, 13.89 c.c. being required. This gives 0.1082 gram of silver in the solution, compared with 0.1077 gram calculated from the strength of the silver nitrate solution used. The results are always rather high, and this is probably due to the escape of hydrogen cyanide during the solution of the silver chloride, which occupies some time. The filter paper does not interfere with the titration. The method, however, is neither so accurate nor so convenient as the gravimetric method (see below).

Gravimetric Determination of Silver in Presence of Mercuric Nitrate.

According to Fresenius (*Quant. Anal.*, 6th German Ed., Vol. I, p. 607), the precipitation of silver as chloride by hydrochloric acid in presence of mercuric nitrate is never complete, owing to the solubility of silver chloride in mercuric nitrate. Even when sufficient hydrochloric acid is added to convert both silver and mercury into chlorides, complete precipitation of the silver cannot be absolutely depended upon. Menshutkin also (*Analyt. Chem.*, Eng. Ed., 1895, p. 339) states that, in presence of mercuric nitrate, the separation of silver as silver chloride is inexact, as the results are affected by the solubility of silver chloride in mercuric nitrate.

In the volumetric method given above, it is necessary that the silver should be completely precipitated as chloride. I therefore carried out a large number of gravimetric estimations of silver as chloride in presence of widely varying quantities of mercuric nitrate, and the results in all cases agreed with those obtained from the same silver nitrate solutions without the addition of mercuric nitrate. The method was the following. To the solution containing silver and mercuric nitrates, which always contained a little free nitric acid, hydrochloric acid was added drop by drop with

stirring. The total quantity of hydrochloric acid added was very slightly in excess of that required to convert both the silver and the mercury into chlorides. The solution containing the precipitate was heated on the water-bath with constant stirring to coagulate the silver chloride, and allowed to cool completely. The clear solution was again tested with a drop of hydrochloric acid to ensure that precipitation was complete. The clear liquid was then decanted through a Gooch's crucible, and the precipitate remaining in the beaker washed several times with dilute nitric acid. The precipitate was transferred to the crucible, washed several times with cold water, and dried at 120°. The following table contains the results of these determinations. The first column gives the weight in grams of silver chloride from 25 c.c. of the silver nitrate solution alone. The second column gives the amount of mercuric nitrate added to 25 c.c. of the same silver nitrate solution as in the first column, and the third column gives the weight of silver chloride precipitated from this mixture. The mercuric nitrate solutions used contained no trace of mercurous salt.

	I.	II.	III.
1.....	0·3598	5 c.c. of 0·1239 <i>N</i> -solution	0·3603
2.....	0·3598	5 „ 0·1559 „	0·3597
3.....	0·3598	10 „ 0·1239 „	0·3599
4.....	0·3598	15 „ 0·1239 „	0·3598
5.....	0·3598	20 „ 0·1239 „	0·3600
6.....	0·3598	15 „ 0·5447 „	0·3601
7.....	0·3598	20 „ 0·5447 „	0·3598
8.....	0·3574	25 „ 0·1239 „	0·3573
9.....	0·3620	25 „ 0·2935 „	0·3622

From these results it appears that the presence of mercuric nitrate does not affect the gravimetric estimation of silver as chloride, provided that the estimation is carried out as described above. The statements of Fresenius and Menschutkin receive no confirmation.

CHEMICAL DEPARTMENT,
UNIVERSITY OF ABERDEEN.

CXCVI.—*A Method for the Measurement of Vapour Pressures.*

By ALEXANDER CHARLES CUMMING.

A NUMBER of methods have been proposed and used for the measurement of vapour pressures, such as those of salt hydrates, but the only one which has found favour with subsequent workers

is the differential tensimeter method. This has been described by Frowein (*Zeitsch. physikal. Chem.*, 1887, **1**, 1), and the apparatus is figured in most text-books of physical chemistry. Although theoretically very simple, it is, in practice, a most unsatisfactory instrument, and for some reason it is very difficult to obtain accurate or even concordant results with it (compare Cohen, *ibid.*, 1894, **14**, 89). Andreae (*ibid.*, 1891, **7**, 241) has drawn attention to one source of error. Since a solution or a hydrate gives up water when the apparatus is evacuated, there is always a certain amount of vapour in the side of the apparatus which contains the substance, and in the other side there will always remain enough air to give a pressure equal to this vapour pressure. Only by long continued evacuation can the last trace of air be removed, but during the process the hydrate is always more or less dehydrated.

Other proposed methods (Pareau, "Pompbarometer," *Inaug. Diss.*, 1875; Linebarger, *Zeitsch. physikal. Chem.*, 1894, **13**, 505; Müller-Erbach, *ibid.*, 1895, **17**, 446) have not been adopted either from difficulties in the manipulation, or on account of inaccuracy. Lescœur (*Ann. Chim. Phys.*, 1889, [vi], **16**, 378; 1890, [vi], **19**, 533, *et seq.*) has used a method which differs completely in principle from any other method. The hydrate was placed in a glass vessel, and after some time the vapour tension in the atmosphere above the hydrate was determined by an ordinary dewpoint method. Many of Lescœur's results are in fair accord with those obtained by other methods, but in some cases there is no agreement, for example, for a saturated solution of decahydrated sodium sulphate at 30.1°, Cohen found the pressure to be 28.03 mm., whilst Lescœur at 30.0° found 24.8 mm. Such differences occur sufficiently often to make it almost certain that there must be some inherent defect in Lescœur's method, and it may be noted that in the twenty years since its publication it has not found application by others.

The author hopes to show in the present paper that it is possible to base an accurate and easy method for the measurement of the vapour tensions of hydrates and solutions on a determination of the dewpoint under certain conditions. As the proposed method resembles that of Lescœur in this respect, some reasons for the inaccuracies in his results will be suggested after a description of the method which has been used.

EXPERIMENTAL.

The principle of the method is to determine the dewpoint in an atmosphere containing vapour in equilibrium with the solution or solid under examination. The apparatus used consisted of a

wide-mouthed glass bottle *B*, which contained a sample of the hydrate or liquid. The bottle was fitted with a rubber cork *D*, through which passed a silver cylinder *A*, closed at the lower end, and a glass tube *C*, provided with a stopcock.

The silver cylinder, which was 2 cm. in diameter and 10 cm. long, was fitted at the top with a three-holed cork, which carried a thermometer and two glass tubes, arranged so that air could be blown through a liquid in the cylinder.

The measurement of the vapour pressure of 44.8 per cent.

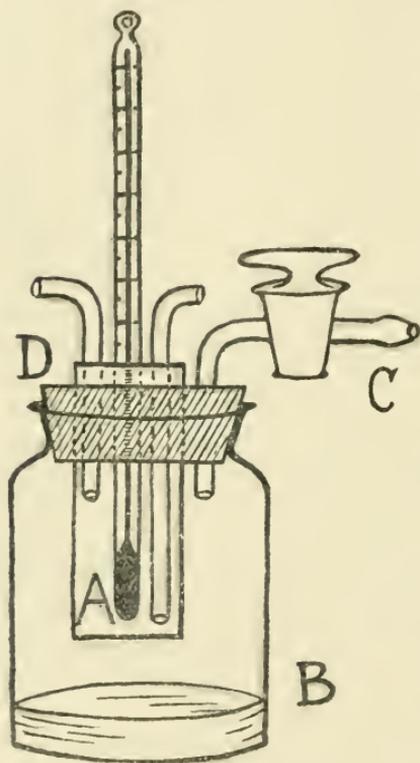
sulphuric acid may be described to illustrate the mode of experiment. About 50 c.c. of the acid were placed in the bottle and the cork *D* inserted. The bottle was exhausted by means of the water-pump through *C*, and the tap closed. The bottle was then placed in a glass-fronted thermostat up to the neck, and kept at 29.8° for some hours.

To find the dewpoint, the silver tube *A* was two-thirds filled with ether, and air blown through at such a rate that the temperature fell very slowly. A dew began to form on the highly-polished silver surface when the thermometer indicated 17.5°. The supply of air was then reduced and the temperature rose slowly, until at 17.7° the last trace of mist on the silver surface had gone. The pressure at 17.6° is from Regnault's* values 15.0

mm. The vapour pressure of 44.8 per cent. sulphuric acid at 29.8° is therefore 15.0 mm.

The method has the marked advantage over other methods that it is practically independent of the degree of exhaustion. It was found that the same result was obtained to 0.1 mm. when the exhaustion was carried out with a water-pump and with a mercury-pump, and identical results were obtained after five, ten, and fifteen minutes' exhaustion with a water-pump.

* Vapour pressures of water and of sulphuric acid solutions are, throughout this paper, taken from Landolt-Börnstein, *Physikalisch-chemische Tabellen* (1905).



Although the vapour pressure is theoretically almost independent of the amount of air, it is expedient to evacuate the apparatus, as otherwise the time required to attain equilibrium may be unduly prolonged.

Further, if more than traces of air are left in the apparatus, an actual error may be introduced by conduction of heat from the outer wall to the silver cylinder. The tubes used were made of silver and highly polished. When any patent polish was used, it was found necessary to clean it off with alcohol before use and polish finally with chamois leather; otherwise the tube quickly became tarnished. Copper tubes were also tried, but were not as satisfactory as the silver tubes.

Objection may be taken to the use of a rubber stopper, but the amount of moisture in rubber corks is very small, and the results show that the error, if any, was negligible. Ordinary corks are obviously unsuitable, on account of the moisture in them.

The method was found very convenient and rapid in practice, and it was desired to ascertain the degree of accuracy attainable.

The vapour pressures of sulphuric acid solutions are probably known with greater accuracy than any other aqueous vapour tensions, and experiments were therefore carried out at various temperatures and with different concentrations.

Vapour Pressure of 44·8 per cent. Sulphuric Acid.

Temperature	19·4°.	20·1°.	25·9°.	29·8°.	30·8°.
Determined by author's method...	8·0	8·1	11·9	15·0	16·0
From Regnault's values	7·8	8·2	11·7	14·9	15·9
,, Sorel's ,,	7·9	8·2	11·8	15·0	16·1

Vapour Pressure of 34·5 per cent. Sulphuric Acid.

Temperature	14·2°.	24·2°.	27·9°.	30·9°.
Determined by author's method ...	8·9	15·1	19·1	22·7
From Regnault's values	8·8	15·3	19·0	22·5

Measurements have also been made in the case of certain salt hydrates, and some of the results are given below. In all cases the salt was free from any appreciable amount of impurity. It was powdered, a portion of it partly dehydrated, and the whole thoroughly mixed.

For the system $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} - \text{CuSO}_4 \cdot 3\text{H}_2\text{O}$, Frowein's figures are, at 20·1°, 4·9 mm.; at 25·9°, 7·8 mm. For the same temperatures my results were 5·2 mm. and 7·8 mm. For the system $\text{MgSO}_4 \cdot 7\text{H}_2\text{O} - \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$, at 20·1°, the pressure found was 7·4 mm., as against 7·7 mm. from Frowein's results. These results are typical of the variations between the pressures found by the

dewpoint method and the results given by Frowein. The differences are small, and in no case has a difference of more than 0.4 mm. been noticed.

It is uncertain what degree of accuracy is attainable with the differential tensimeter method as used by Frowein. Andreae (*loc. cit.*) has shown that in ordinary use a trace of air is left, but that air could be completely removed by evacuation while the bulbs of the apparatus were immersed in solid carbon dioxide. The magnitude of the error introduced by neglect of this trace of air will vary with the amount of moisture given off by the hydrate, the rate at which it is given off, and other details of the particular experiment. It is difficult, therefore, to assign even a probable value to the experimental error involved in results such as those of Frowein.

As an indication of the magnitude of the possible error from residual air, it may be mentioned that Andreae found it to be 0.2 to 0.3 mm. in his experiments. A comparison of results with those of Andreae was not attempted, as his measurements were made on the differences in vapour pressure between different hydrates, and do not include the actual vapour pressures of single hydrates. The results obtained with sulphuric acid solutions prove that the dewpoint method is accurate.

It was found that the equilibrium pressure was quickly attained with solutions, and that more time was required for solid hydrates. All the solutions so far examined have reached their equilibrium pressure within an hour. The vapour pressure of a salt hydrate does not usually become constant so quickly, and in some cases a steady value is only obtained after one or more days. It was found, particularly in the case of salt hydrates, that a slight error is introduced if the readings succeed one another at all quickly, and a reason for this may be suggested. When water is condensed on the surface of the silver tube, the pressure in the apparatus is reduced, and more vapour is supplied by the hydrate. The film of moisture is vaporised when the tube is warmed, and time must therefore be allowed for equilibrium to be re-established before another reading is taken. With very slow alteration in the temperature of the silver tube, and with an hour or more between readings, it was found that variations between readings rarely exceeded 0.1°. A difference of 0.1° at 0° is equivalent to a difference of 0.03 mm.; at 10° to a difference of 0.06 mm.; and at 20° to a difference of 0.11 mm. An accuracy of 0.1 mm. was regarded as quite sufficient for present purposes. It is the intention of the author to endeavour to obtain a more delicate apparatus, but the method as outlined above is sufficiently accurate for most

purposes, and a higher degree of accuracy means a corresponding sacrifice in simplicity and speed.

Lescœur appears to have taken little trouble to keep the temperature constant, since he states that the vessel was kept in a room the temperature of which did not vary more than 5° from the temperature given.

In later experiments, he applied a correction by calculation when the apparatus was not at the desired temperature. In his experiments, the apparatus was not evacuated, and serious errors may arise from this cause, particularly in cases where a long time is required to attain the equilibrium pressure. In any case, it must be better to remove most of the air, since the vapour pressure in the immediate neighbourhood of the apparatus might otherwise differ largely from that in other parts of the apparatus. There are other minor sources of error, but the above are sufficient to account for his results. It should be mentioned that in many, and perhaps in most, cases, Lescœur's results will prove to be accurate, but as the matter stands it is not known which results are trustworthy.

The dewpoint method is particularly suited to the measurement of aqueous vapour tensions, but it may also be applied to the measurement of other vapour pressures.

It is to be applied to the measurement of vapour tensions required in another investigation, and the author hopes to obtain also a comparison of results for the vapour pressure of some salt hydrates measured by the above method and by an accurate differential tensimeter method.

CHEMISTRY DEPARTMENT,
UNIVERSITY OF EDINBURGH.

CXCVII.—*Some Mercury Derivatives of Camphor.*

By JAMES ERNEST MARSH and ROBERT DE JERSEY FLEMING
STRUTHERS.

IN this paper an account is given of experiments made during the past two years, some of the results of which have already been briefly recorded (Proc., 1907, **23**, 246; 1908, **24**, 267). The work is a consequence of the observation that an alkaline solution of mercuric cyanide gives with acetone an insoluble mercury derivative (Trans., 1905, **87**, 1878). We obtained similar derivatives of other ketones, but only with those which have a methyl group attached

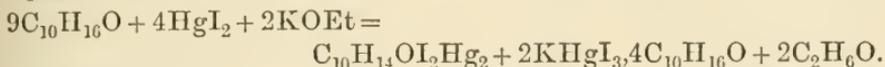
to the carbonyl group. By using mercuric iodide instead of mercuric cyanide, mercury derivatives of other ketones are obtained, provided that the ketones contain hydrogen in the α -position with respect to the carbonyl group. We have prepared in this way mercury derivatives of acetone, acetophenone, diethyl ketone, and camphor, but not of benzophenone or fenchone. This reaction has been studied mainly so far as it concerns camphor. We have subjected camphor to the action of mercuric iodide in presence of an alcoholic solution of potassium ethoxide and of an aqueous solution of potassium hydroxide with and without the addition of potassium iodide, and with and without the action of heat. By the action of potassium ethoxide, and by the action of a cold aqueous solution of potassium hydroxide, dimercuriccamphor diiodide, $C_{10}H_{14}OHg_2I_2$, is formed. On the other hand, by employing heat, an aqueous solution of potassium hydroxide gives, in presence of excess of potassium iodide, a more condensed compound, namely, tetramercuritricamphor diiodide, $(C_{10}H_{14}O)_3Hg_4I_2$. Further, in the hot solution, we have obtained evidence of the formation of the compound $(C_{10}H_{14}O)_4Hg_5I_2$ when the potassium iodide is not in excess, and of the compound $(C_{10}H_{14}O)_5Hg_6I_2$ when the potassium iodide is in defect.

EXPERIMENTAL.

Action of Mercuric Iodide on Camphor in Presence of Potassium Ethoxide.

When mercuric iodide is added to a solution of sodium or potassium ethoxides in alcohol, the red colour of the iodide disappears, and a pale yellow precipitate takes its place. If, however, camphor is dissolved in the solution, the mercuric iodide dissolves without giving any precipitate. 1.5 Grams of potassium were dissolved in 50 c.c. of absolute alcohol, 9 grams of camphor were then added, and, by degrees, 13.5 grams of mercuric iodide. A clear solution was obtained, which was poured into water, giving a white precipitate. The mixture was then saturated with carbon dioxide to prevent reduction to metallic mercury, which is brought about by the action of alcohol on an aqueous alkaline solution of mercuric iodide. The precipitate was collected, washed with water, and dried, to remove excess of camphor. It was then digested with an aqueous solution of potassium iodide to remove excess of mercuric iodide, and again washed and dried. It weighed 6.5 grams. The above-described treatment is necessary for the removal of the double salt, $KHgI_3 \cdot 4C_{10}H_{16}O$ (described at the end of this paper), which is formed from its constituents in alcoholic

solution. The quantities taken were in accordance with the equation:



Dimercuricamphor di-iodide was obtained as a nearly colourless, amorphous powder. It is insoluble in alcohol, and its solubility in the liquid when it is prepared is explained later. We have obtained it in a purer form by two other methods. When prepared by the above-mentioned method, its analysis gave a low value for mercury and a high value for the other constituents. This is doubtless due to the difficulty of getting rid entirely of the double salt, which retains camphor even when heated for some time:

Found, C=15.4; H=1.9; I=31.8; Hg=48.0.

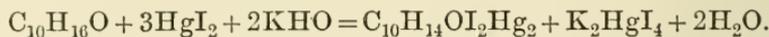
$C_{10}H_{14}OI_2Hg_2$ requires C=14.9; H=1.7; I=31.5;
Hg=49.7 per cent.

A solution of sodium ethoxide in alcohol reacted in a precisely similar way. An alcoholic solution of potassium hydroxide, however, acted rather differently. In this case, the mercuric iodide did not readily pass into solution, and reduction to metallic mercury appeared to take place.

Action of a Cold Aqueous Solution of Potassium Hydroxide on Mercuric Iodide and Camphor.

When a cold solution of potassium hydroxide acts on mercuric iodide alone, there is a certain amount of decomposition, with formation of potassium iodide and a basic mercuric iodide, without apparent change in the colour or density of the precipitate. In presence of sufficient camphor, however, the red powder gradually disappears, and its place is taken by a pale yellow precipitate, which is specifically lighter. The method of preparation was as follows. Fifty c.c. of *N*-potassium hydroxide were mixed with 6.7 grams of mercuric iodide, and a solution of 0.75 gram of camphor in a little petroleum added. The whole was then mechanically shaken for several hours until the red powder had disappeared, and its place was taken by a nearly colourless precipitate. The point when the reaction is finished is easy to determine, as the precipitate is fairly light, and the heavy red powder is seen below it as long as any is present. The reaction is hastened by using a more concentrated solution of potassium hydroxide. The mixture was then freed from petroleum in a vacuum, filtered, washed, and dried. The precipitate thus obtained does not appear to be a single substance, and its composition varies according to the proportions of the materials used. The amounts of mercury and iodine in different

samples has varied from 50.1 to 53.6 per cent. of mercury and 28.5 to 24.7 per cent. of iodine. The product with the lower percentage of mercury was obtained by employing only 4.5 grams of mercuric iodide. The yield was fairly constant, being about 5 grams for every gram of camphor used with the full amount of mercuric iodide. The amounts were taken in accordance with the following equation:



According to this equation, two-thirds of the total mercury and one-third of the total iodine should be found in the precipitate, whilst there was actually found two-thirds of the total mercury, but only one-quarter of the total iodine. It seems not unlikely that the precipitate consisted mainly of the compound $\text{C}_{10}\text{H}_{14}\text{O} \cdot \text{Hg}_2\text{I}_2$, together with a certain variable amount of a compound, $\text{C}_{10}\text{H}_{14}\text{O} \cdot \text{Hg}_2\text{O}$. This view receives support from the action of a solution of potassium iodide on the substance; the solution at once becomes alkaline, and by repeating the treatment dimercuric camphor di-iodide is obtained. On analysis:

Found, I = 31.7; Hg = 49.2.

$\text{C}_{10}\text{H}_{14}\text{OI}_2\text{Hg}_2$ requires I = 31.5; Hg = 49.7 per cent.

Since potassium hydroxide gives no precipitate with a solution of mercuric iodide in potassium iodide, it was thought that the dimercuric camphor iodide might be obtained pure by using the compound K_2HgI_4 in the alkaline solution. No action at all was observed in the cold, even after several months, with this mixture. Action, however, readily takes place when the mixture is heated on a water-bath, but with the formation of a different compound.

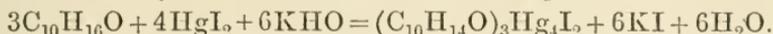
Action of an Alkaline Solution of the Compound K_2HgI_4 on Camphor at 100°.

Camphor, dissolved in a little petroleum, was heated with an alkaline solution of the compound K_2HgI_4 on a water-bath. It was ascertained that the alkaline solution had no action on the petroleum alone. With the camphor, in a short time a yellow precipitate began to form, and gradually increased in quantity. The action was allowed to proceed for twenty-four hours or longer. The precipitate was then collected, washed, and dried at 100° to remove water and camphor. The amount of alkali employed was about 100 c.c. of 33 per cent. potassium hydroxide for every 10 grams of camphor. The amount of mercuric iodide was varied in different experiments, and in each case was dissolved in the

requisite amount of potassium iodide. The yield (in grams) is given in the following table:

Camphor.	Mercuric iodide.	Precipitate.	
		Found.	Calculated.
10	16·6	13·3	14
10	27·5	17·5	22
10	30	19	25
10	45	22	33

The calculated yield is obtained from the equation:



Accordingly, every 10 grams of camphor should require 40 grams of mercuric iodide, and give 33 grams of the compound. It is seen that the yield approaches nearest to the theoretical amount when the camphor is in the greatest excess. The precipitate, even after prolonged washing, retains from two to three per cent. of fixed mineral matter. Ignition left potassium iodide, but extraction with a large bulk of water gave, after evaporation, not iodide, but carbonate. It was estimated as potassium sulphate by ignition with sulphuric acid. Analysis of the precipitate gave: I=16·6; Hg=51·6; K₂CO₃=2·5. If we allow for the 2·5 per cent. of impurity, the composition is:

Found, I=17·0; Hg=52·9.

C₃₀H₄₂O₃I₂Hg₄ requires I=16·9; Hg=53·2 per cent.

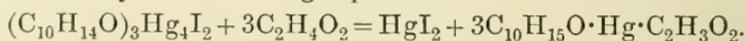
The method of preparation just described requires a considerable amount of potassium iodide, and since this iodide is also found in the reaction, there is eventually much more of it than is necessary to keep the mercury iodide in solution. It is probable that it is this large amount of potassium iodide which tends to prevent the completion of the reaction. The plan was therefore tried of making the experiment progressive, namely, by starting with small amounts of camphor, the compound K₂HgI₄, and alkali, and adding continually fresh charges of camphor, mercuric iodide, and alkali. In this way, the original potassium iodide, together with that formed in the reaction, serves to dissolve the mercuric iodide if it is not added too quickly, or in too large a quantity at a time. Starting with 6·6 grams of potassium iodide, we obtained from 15 grams of camphor and 45 grams of mercuric iodide, added in five stages, 36 grams (theory=37) of the compound. In another experiment, using 2 grams of potassium iodide, then 21 grams of camphor and 63 grams of mercuric iodide in 13 stages, we obtained 49 grams (theory=51) of the precipitate. The yield will be seen to be much better than in the earlier experiments, and, in fact, leaves nothing to be desired. The composition of the precipitate was also found to be the same:

Found, I=16·7; Hg=51·2; K₂CO₃=2·2.

In this case also, potassium iodide still accumulates in the mother liquor. Thus, in the second experiment, the 49 grams of precipitate contained 25 grams of mercury and 8.5 grams of iodine. The 63 grams of mercuric iodide employed contained 27.7 grams of mercury and 35.3 grams of iodine. Hence the solution, which at starting only contained 2 grams of potassium iodide, will in the end contain 32 grams, and only 6 grams of mercuric iodide. This accumulation of potassium iodide may be prevented by employing as the fresh charges a mixture of mercuric iodide and chloride or a mixture of potassium iodide and mercuric chloride. It was not found possible to obtain any mercury derivative of camphor by the use of mercuric chloride alone, but the addition of a very small quantity of potassium iodide was sufficient to start the reaction. With defect of potassium iodide the compound is mixed with mercuric oxide. The substance $(C_{10}H_{14}O)_3Hg_4I_2$ was obtained as a pale yellow, amorphous powder. It is scarcely affected by the ordinary solvents; alcohol has a slight solvent action, and carbon disulphide partly dissolves it without separating it into any simpler constituents. It is slowly attacked and decomposed by an aqueous solution of potassium iodide, and is rapidly decomposed by potassium iodide in acetone solution. The halogen and hydrocyanic acids readily decompose it into camphor and a mercuric salt. The diluted oxygen acids have little or no action. Concentrated nitric acid oxidises it, giving camphoric acid, melting at 186° (anhydride, m. p. 220°); concentrated sulphuric acid decomposes it, with separation of mercuric iodide. A more complete study of the action of glacial acetic acid was made.

Action of Glacial Acetic Acid on the Compound $(C_{10}H_{14}O)_3Hg_4I_2$.

When the compound is heated with glacial acetic acid, the whole dissolves, and, on cooling, mercuric iodide crystallises out. The filtrate gives a clear mixture with water, and on evaporation dries to a colourless, transparent glass. It was not obtained in a form suitable for analysis, but the experiments recorded below leave no doubt that it is the acetate of mercuriccamphor, $C_{10}H_{15}O \cdot Hg \cdot O \cdot CO \cdot CH_3$. The action of the hot acetic acid may be represented by the following equation:



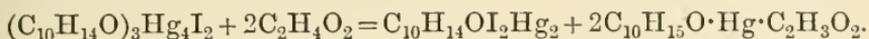
When cold glacial acetic acid acts on the compound, a different reaction takes place. The yellow colour of the compound disappears, and a white precipitate and a colourless solution result. The change is complete in about an hour. It suggests by its appearance, not the extraction of a coloured from a colourless constituent in a mixture, but rather the occurrence of a definite

reaction. After an hour or longer, the precipitate was collected, washed, and dried. It was analysed, and found to be dimercuricamphor di-iodide, $C_{10}H_{14}OHg_2I_2$:

Found, C=14·7; H=1·9; I=31·3; Hg=49·0.

$C_{10}H_{14}OI_2Hg_2$ requires C=14·9; H=1·7; I=31·5;
Hg=49·7 per cent.

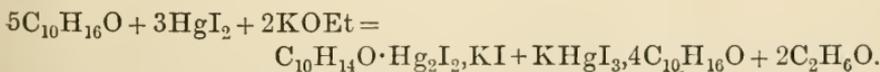
The filtrate, on dilution with water, gave a slight further precipitate. The solution resembled closely, especially in its reaction with potassium iodide, the similar solution obtained with hot acetic acid. On the supposition, therefore, that it contains mercuricamphor acetate, the following equation represents the action of cold acetic acid:



The theoretical yield of dimercuricamphor di-iodide is accordingly 53 per cent. In two experiments, we found 50 and 52 per cent. respectively, this being the total precipitate after adding water.

Dimercuricamphor di-iodide is a colourless, amorphous powder, insoluble in water and other neutral solvents. It can be sublimed without melting, and without apparent decomposition. It is not dissolved or decomposed by an aqueous solution of potassium iodide. Whilst neither alcohol nor acetone dissolve the substance, a mixture of it and potassium iodide in molecular proportions is readily soluble in alcohol, and almost without limit in acetone. These observations show that the dimercuricamphor di-iodide is not present as such in the original substance, since both an aqueous solution of potassium iodide and acetone and potassium iodide decompose that substance. Hence the original substance is not a mixture containing dimercuricamphor di-iodide as a constituent, but is most probably a definite compound.

There is no reason to suppose that the dimercuricamphor di-iodide obtained in this way is a different compound from that obtained by the action of potassium ethoxide or of a cold solution of potassium hydroxide on a mixture of camphor and mercuric iodide. It was at first thought that the compound produced by the action of potassium ethoxide was different because it gave a clear solution in alcohol. But since potassium iodide is formed at the same time, the substance dissolved is not dimercuricamphor di-iodide, but the double salt, $C_{10}H_{14}O \cdot Hg_2I_2 \cdot KI$, which, as previously mentioned, is readily soluble in alcohol. Probably the equation explaining the action of potassium ethoxide is best represented as:



Here both the double salts are soluble in alcohol.

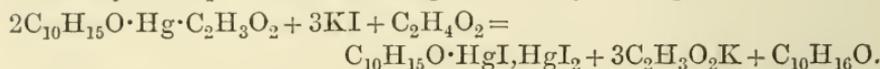
Mercuricamphor Iodide, $C_{10}H_{15}O \cdot HgI$, and its Double Salt,
 $C_{10}H_{15}O \cdot HgI, HgI_2$.

The solution obtained by the action of glacial acetic acid on the original substance, and presumed to contain mercuricamphor acetate, was, after dilution with water, treated with a solution of potassium iodide, when a thick, yellow precipitate was formed. This precipitate redissolved with excess of potassium iodide, being thereby decomposed. The addition of potassium iodide was stopped when it ceased to give any further precipitate, and the orange-yellow substance was collected. It proved to be a double salt of mercuricamphor iodide with mercuric iodide, of the formula $C_{10}H_{15}O \cdot HgI, HgI_2$, which was not quite pure. Analysis gave:

Found, C=13·0; H=1·9; I=38·4; Hg=42·6.

$C_{10}H_{15}OI_3Hg_2$ requires C=12·9; H=1·6; I=40·8;
 Hg=42·9 per cent.

It may be represented as being formed by the equation:



It will be seen that in order to obtain this compound, mercuric iodide has to be formed at the expense of the camphor compound. To prevent this, a solution of mercuric iodide in potassium iodide was used to precipitate the compound, with the effect of more than doubling the yield of it. Although potassium iodide in the acetic acid solution decomposes the compound with separation of camphor, in neutral solution it only removes the mercuric iodide from the double salt without decomposing it further. In this way, mercuricamphor iodide, $C_{10}H_{15}O \cdot HgI$, is left as a nearly colourless precipitate. It was washed, dried, and analysed:

Found, C=24·8; H=3·2; I=26·5; Hg=42·0.

$C_{10}H_{15}OIHg$ requires C=25·1; H=3·1; I=26·5;
 Hg=41·8 per cent.

Mercuricamphor iodide is soluble in ethyl acetate, and crystallises from it in very minute, colourless crystals, melting at 184°. It is decomposed by glacial acetic acid. The deficiency of iodine in the analysis of the double salt is probably due to the removal of some mercuric iodide from it by using a slight excess of potassium iodide. The same cause has raised the amount of carbon without appreciably affecting the percentage of mercury.

Mercuricamphor Bromide, $C_{10}H_{15}O \cdot HgBr$.

Ten grams of the compound $(C_{10}H_{14}O)_3Hg_4I_2$ were treated with 15 c.c. of cold glacial acetic acid for one hour, then diluted with

water, and filtered. To the filtrate was added a solution of potassium bromide in water, as long as it gave a precipitate. 1.3 Grams of potassium bromide were required. The white precipitate was collected, washed, and dried. It weighed 4.5 grams (theory = 5.7):

Found, Br = 18.2; Hg = 45.8.

$C_{10}H_{15}OBrHg$ requires Br = 18.5; Hg = 46.4 per cent.

Mercuricamphor bromide is insoluble in water, but readily soluble in glacial acetic acid, from which it separates in colourless, transparent crystals, melting at 220—221°. It is soluble to a certain extent in dilute acetic acid; hence the full amount is not precipitated when potassium bromide is added to the acid solution.

Mercuricamphor Chloride, $C_{10}H_{15}O \cdot HgCl$.

As before, 10 grams of the compound $(C_{10}H_{16}O)_3Hg_4I_2$ were digested for one hour with cold glacial acetic acid, and the mixture was diluted with water and filtered. The filtrate was precipitated by the gradual addition of a solution of sodium chloride; 0.7 gram of sodium chloride was just in excess. The precipitate, after washing and drying, weighed 4 grams, whilst theory requires 5 grams [$(C_{10}H_{14}O)_3Hg_4I_2$ gives $2C_{10}H_{15}O \cdot HgCl$], and the amount given by 0.7 gram of sodium chloride should be 4.8 grams. The chloride, although insoluble in water, is sparingly soluble in dilute acetic acid. It crystallises well from glacial acetic acid. Before crystallisation it melted at 219°, and afterwards at 222°:

Found, Cl = 9.2; Hg = 51.8.

$C_{10}H_{15}OClHg$ requires Cl = 9.2; Hg = 51.7 per cent.

Professor Bowman reports on the crystals as follows: "Mostly aggregates of flattish needles, with pointed ends, having a longitudinal cleavage. The material is biaxial, and small crystals and cleavage flakes show under the microscope a division into two halves by a longitudinal twin junction. The extinction is nearly straight. Through each half emerges a single optic axis inclined slightly in the plane transverse to the needles. The crystals show only imperfect extinction between crossed Nicols, and appear to consist of overlapping lamellæ. The double refraction is moderate, and is compensated by a quartz wedge inserted parallel to the length of the needles."

Mercuricamphor Oxide, $(C_{10}H_{15}OHg)_2O$.

The existence of the iodide, bromide, and chloride of mercuricamphor indicated the possibility of obtaining the base or oxide, of which they may be regarded as salts. This base was obtained

by precipitating the acetate with pure sodium hydroxide. It is necessary for this purpose that the hydroxide should contain no chloride; if it does, the chloride is precipitated along with the base.

Seven grams of the compound $(C_{10}H_{14}O)_3Hg_4I_2$ were digested for an hour with 15 c.c. of cold glacial acetic acid, the mixture being then diluted with water, and filtered. The filtrate was mixed with 100 c.c. of 10 per cent. pure sodium hydroxide, when a white, granular precipitate was formed, which, when washed and dried, weighed 2.3 grams (theory=3.3). The base is probably slightly soluble in water, as potassium iodide gave a precipitate with the solution from which the base had been separated:

Found, C=33.1; H=4.1; Hg=55.4.

$C_{20}H_{30}O_3Hg_2$ requires C=33.4; H=4.2; Hg=55.7 per cent.

The oxide is readily soluble in alcohol or carbon disulphide, but does not crystallise. From carbon disulphide it is left, on evaporation, as a clear, transparent glass. On heating above 100° , it loses camphor, with formation apparently of the oxide $(C_{10}H_{14}O)_2Hg_3O$. From the base by the action of acids, and from the chloride by double decomposition, other salts of mercuricamphor have been prepared, for example, the sulphate, nitrate, oxalate, and benzoate, but have not as yet been completely examined.

*Action of Iodine on the Compound $(C_{10}H_{14}O)_3Hg_4I_2$:
Di-iodocamphor.*

Twelve grams of the mercuricamphor compound were treated with a cold solution of 8 grams of iodine in benzene. Mercuric iodide soon began to separate, and when the action was apparently finished, the filtered solution was evaporated in a current of carbon dioxide in the dark. Pale yellow, hard crystals separated, which weighed 6 grams (theory=8 grams). The substance was recrystallised from petroleum, when it melted at 109° . Analysis showed it to be di-iodocamphor:

Found, C=30.6; H=3.9; I=62.7.

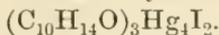
$C_{10}H_{14}I_2$ requires C=29.7; H=3.5; I=62.8 per cent.

The rotation in 2.8 per cent. chloroform solution was about $[\alpha]_D + 28^\circ$, but the accurate determination was difficult, owing to the separation of iodine.

Di-iodocamphor decomposes on keeping, especially in a closed bottle; it is more stable when freely exposed to air. Its solution in petroleum or chloroform gives free iodine on exposure to light, and its solution in petroleum also becomes coloured by iodine on

warming. The production of di-iodocamphor in this way shows that in the original substance two hydrogen atoms of the camphor have been replaced by mercury.

Action of Aqueous Potassium Hydroxide on the Compound



By heating the compound $(C_{10}H_{14}O)_3Hg_4I_2$ with potassium hydroxide containing potassium iodide on a water-bath, a substance containing 12 to 13 per cent. of iodine was formed. Further, by prolonged heating with potassium hydroxide and removing the alkali whenever it was found to contain iodine, a compound free from iodine was eventually obtained. This substance, which is colourless, has the composition represented by the formula $(C_{10}H_{14}O)_2Hg_3O$:

Found, C = 26.1; H = 3.2; Hg = 64.4.

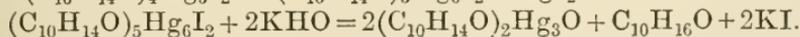
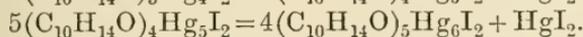
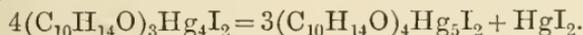
$C_{20}H_{28}O_3Hg_3$ requires C = 26.2; H = 3.0; Hg = 65.5 per cent.

We have obtained compounds poorer in iodine similar to those mentioned above by diminishing the amount of potassium iodide used in the preparation of the original substance. For example, when mercuric chloride was employed with very little potassium iodide (3 grams of camphor, 5.3 grams of mercuric iodide, and 1 gram of potassium iodide), alcohol extracted from the product of the reaction a substance closely agreeing in composition with the formula $(C_{10}H_{14}O)_5Hg_6I_2$:

Found, I = 11.3; Hg = 54.1.

$C_{50}H_{70}O_5I_2Hg_6$ requires I = 11.5; Hg = 54.4 per cent.

Hence it seems likely that the action of potassium hydroxide and iodide on the substance $(C_{10}H_{14}O)_3Hg_4I_2$ is, in the first place, to form the more highly condensed compounds $(C_{10}H_{14}O)_4Hg_5I_2$, which contains 13.7 per cent. of iodine, and $(C_{10}H_{14}O)_5Hg_6I_2$; and that the latter compound is decomposed by the action of the potassium hydroxide in accordance with the following equations:



The condensation of camphor with mercuric iodide in presence of alkali takes place, in the first instance, with formation of the compound $C_{10}H_{14}OHg_2I_2$. On heating, a further condensation occurs, with the formation of the compound $(C_{10}H_{14}O)_3Hg_4I_2$, and there is evidence of the probable existence of the compounds $(C_{10}H_{14}O)_4Hg_5I_2$ and $(C_{10}H_{14}O)_5Hg_6I_2$. The compound $(C_{10}H_{14}O)_2Hg_3I_2$ in the series is missing, but is represented by the compound $(C_{10}H_{14}O)_2Hg_3O$. The mercury in all the compounds

investigated and described in this paper appears in the mercuric state. In no case when the compounds have been decomposed by a halogen acid has the mercury separated as a mercurous salt.

Double Salt of the Compound KHgI_3 with Camphor of Crystallisation, $\text{KHgI}_3 \cdot 4\text{C}_{10}\text{H}_{16}\text{O}$.

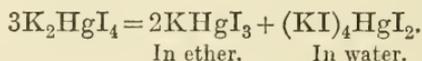
Mercuric iodide dissolves in water containing two molecular proportions of potassium iodide for every one of mercuric iodide. In certain organic solvents, such as ethers, mercuric iodide dissolves along with one molecular proportion of potassium iodide; that is, as the salt KHgI_3 , instead of K_2HgI_4 . Consequently, when an aqueous solution of the latter is shaken with ethyl acetate or ethyl formate, the salt KHgI_3 is dissolved, and if the solution is fairly concentrated, the ethereal solution becomes heavier than the aqueous, and sinks to the bottom. The salt, after evaporation of the ethyl formate, was analysed:

Found, $\text{HgI}_2 = 73.0$; $\text{KI} = 26.9$.

KHgI_3 requires $\text{HgI}_2 = 73.2$; $\text{KI} = 26.8$ per cent.

The same salt was also obtained from ethyl acetate. An experiment was made to ascertain to what extent the salt K_2HgI_4 is decomposed when its aqueous solution is shaken with an ester.

3.3 Grams of potassium iodide and 4.5 grams of mercuric iodide were dissolved in 10 c.c. of water, and the solution shaken with 10 c.c. of ethyl acetate. The lower ester layer gave on evaporation 4.3 grams of the salt KHgI_3 , and the upper aqueous layer gave 3.5 grams of a mixture of potassium iodide, with a little mercuric iodide. The numbers are fairly in accordance with the following equation:



When a solution of camphor in alcohol is added to an aqueous solution of mercuric iodide in potassium iodide, oily drops soon begin to form on the surface of the liquid, and after a time solidify to a mass of crystals. The crystals are hard, not at all of a camphor-like nature, and are of a pale yellow colour. Analysis showed that they had the composition $\text{KHgI}_3 \cdot 4\text{C}_{10}\text{H}_{16}\text{O}$:

Found, Camphor = 49.5; $\text{HgI}_2 = 36.9$; $\text{KI} = 13.5$.

$\text{C}_{40}\text{H}_{64}\text{O}_4\text{I}_3\text{HgK}$ requires Camphor = 49.5; $\text{HgI}_2 = 36.9$;
 $\text{KI} = 13.5$ per cent.

When camphor, mercuric iodide, and potassium iodide are dis-

solved in a moderate amount of alcohol, in the proportions indicated by the formula, the whole sets to a mass of crystals. The crystals are quite stable unless exposed for some time to the air, when they lose their crystalline form and crumble to powder. Their melting point is 65° , and their rotatory power is that of the camphor contained in them.

UNIVERSITY LABORATORY,
OXFORD.

CXCVIII.—*Optically Active Substances Containing no Asymmetric Atom. 1 - Methylcyclohexylidene - 4-acetic Acid.*

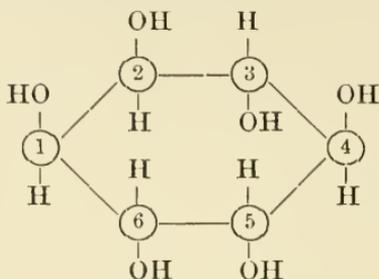
By WILLIAM HENRY PERKIN, WILLIAM JACKSON POPE, and
OTTO WALLACH.

A PERUSAL of van't Hoff's early work on optical activity makes it clear that he adopted the view, first advanced by Pasteur, that the optical activity of amorphous substances is due to enantiomorphism of molecular configuration. Van't Hoff and Le Bel developed Pasteur's conclusion by introducing a definite theory of the configuration of carbon compounds, and showed that the enantiomorphism of molecular configuration possessed by all known optically active substances could be correlated with the presence of asymmetric carbon atoms in the molecule.

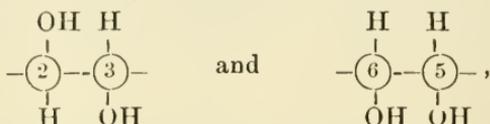
The optical activity is, in fact, not, as is still sometimes stated, due to the presence of an asymmetric carbon atom, but originates in the enantiomorphous molecular configuration. The identification of a particular carbon atom in the molecule as asymmetric is merely a convenient method for recognising enantiomorphism of molecular configuration.

Van't Hoff realised that organic substances are capable of formulation which, whilst possessing enantiomorphous molecular configurations, contain no asymmetric atom, and quoted, as an instance, the formula $\begin{matrix} R_1 \\ R_2 \end{matrix} > C : C < \begin{matrix} R_3 \\ R_4 \end{matrix}$ as that of a substance which should be of enantiomorphous molecular configuration, and therefore capable of exhibiting optical activity in the amorphous state, although its molecule contains no asymmetric atom.

The statement is sometimes made that inosite, which is optically active in solution and has the configuration



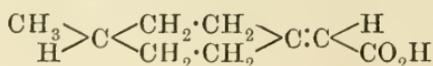
contains no asymmetric carbon atom. This, however, seems to involve a misapplication of the definition of an asymmetric carbon atom. The carbon atom (1) is separately attached to the two systems,



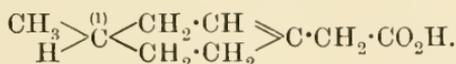
which differ configurationally in the same way respectively as do the *d*-tartaric and mesotartaric acids; although these two groups thus differ in configuration, they are not enantiomorphously related. The carbon atom (1) being attached to these two configurationally dissimilar groups and to two others, namely, H and OH, is directly joined to four quite dissimilar groups, and is hence asymmetric; in the same way, it will be seen that the other five carbon atoms in the inosite molecule are also asymmetric.

No case has, in fact, been experimentally realised of a substance exhibiting optical activity in the amorphous state and containing no asymmetric carbon (nitrogen, sulphur, selenium, tin, or silicon) atom.

In view of the theoretical importance attaching to the discovery of substances exhibiting optical activity in the amorphous condition, and hence possessing enantiomorphous molecular configurations, but containing no asymmetric atom, it appeared desirable to attempt, by modern synthetic methods, the preparation of such compounds. The study of allene derivatives such as were considered by van't Hoff presented obvious disadvantages; the facility with which such substances undergo isomeric change and become converted into acetylene derivatives, and their tendency to combine with water, etc., to yield ethylene derivatives, might be expected to introduce experimental difficulties which would be desirably avoided. Perkin and Pope (*Proc.*, 1906, 22, 107; *Trans.*, 1908, 93, 1075) therefore synthesised the 1-methyl-*cyclohexylidene*-4-acetic acid,



which contains no asymmetric carbon atom, but which, in accordance with the van't Hoff conception, possesses an enantiomorphous molecular configuration, and attempted its resolution into optically active components. By a curious coincidence, Marckwald and Meth were at the same time engaged upon the synthesis of the same compound for the same purpose; they obtained an acid, melting at 40—41°, to which they assigned the constitution given above and effected its resolution into optically active components (*Ber.*, 1906, 39, 1171). The acid melting at 40—41° was, however, quite different from that prepared by Perkin and Pope, which melts at 66°,* and the latter authors suggested (*Proc.*, 1906, 22, 107) that Marckwald and Meth's acid is the isomeric 1-methyl- Δ^3 -cyclohexene-4-acetic acid of the constitution



As the carbon atom numbered (1) in the latter constitutional formula is obviously attached to four constitutionally dissimilar groups it is asymmetric in the ordinary sense; the resolution of such a synthetic product into optically active components therefore merely illustrates again the optical activity of substances which contain an asymmetric carbon atom in the molecule.

The difference of opinion briefly referred to above gave rise to a long controversy, and led to an extended series of experimental investigations (Marckwald and Meth, *Ber.*, 1906, 39, 1171, 2035, 2404; Wallach, *Annalen*, 1907, 313, 311; 1909, 365, 255; Perkin and Pope, *Trans.*, 1908, 93, 1075; Harding, Haworth, and Perkin, *Trans.*, 1908, 93, 1943; Hope and Perkin, *Trans.*, 1909, 95, 1360) The final result of this work has been to prove conclusively that the original view taken by Perkin and Pope was correct; the acid melting at 66° is the true 1-methylcyclohexylidene-4-acetic acid, whilst the acid melting at 40—41°, which Marckwald and Meth supposed to be the latter acid, is the 1-methyl- Δ^3 -cyclohexene-4-acetic acid, the graphic formula of which contains an asymmetric carbon atom. The resolution effected by Marckwald and Meth thus failed to yield a substance exhibiting optical activity and containing no asymmetric atom.

The close study devoted to the two isomeric acids under discussion led to simplifications in the preparation of 1-methylcyclohexylidene-4-acetic acid (Wallach, *Annalen*, 1909, 365, 266), so that large quantities of this acid could be readily obtained for subjection to the treatment usually employed for the resolution of externally compensated acids into their optically active components. Owing to peculiarities in the behaviour of the substance, its resolution presented considerable difficulty, but we ultimately succeeded in separating the *d*- and

* The melting point, 70°, originally given is somewhat too high.

It is thus seen that, even when a highly symmetrical configuration is attributed to methane derivatives, the configuration assignable to 1-methylcyclohexylidene-4-acetic acid possesses neither planes, axes, nor a centre of symmetry. The absence of all these elements of symmetry is more than is requisite to determine the enantiomorphism of the configuration.

From the above discussion it will be observed that the configuration of 1-methylcyclohexylidene-4-acetic acid is enantiomorphous, even under the highly symmetrical condition represented by placing the carbon atoms numbered 1 to 8 and the hydrogen atom (*c*) in the plane of the paper and the carbon atom numbered 9 and the hydrogen atom (*a*) in the plane, perpendicular thereto, referred to above. The enantiomorphism would indeed persist if the hydrogen atoms (*a*) and (*c*) and the carbon atoms 8 and 9 were centred at the apices of a regular tetrahedron.

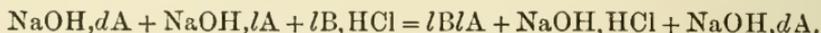
The conviction that the structural formulæ assigned to chemical substances imitate with considerable approximation to truth the real nature of molecular constitution was appreciably deepened by the introduction of the theory of the configuration of methane derivatives by van't Hoff and Le Bel; the development of the theory by Wislicenus, so as to embrace the configuration of ethylene derivatives, and by von Baeyer, in connexion with polymethylene derivatives, has strengthened the view that the constitutional formulæ of organic chemistry represent very closely the actual atomic arrangement of molecular complexes. The considerations which led to the work described in the present paper involved, as has been seen, the development of the original simple geometrical conception of the space configuration of methane and ethylene derivatives to an extent which may appear extreme. The fact that we have been able to show a close correspondence between the anticipations thus derived and the experimental results must be regarded as an independent demonstration of the fidelity with which constitutional formulæ picture molecular constitutions.

Resolution of 1-Methylcyclohexylidene-4-acetic Acid.

The resolution of externally compensated 1-methylcyclohexylidene-4-acetic acid into its optically active components is attended with some difficulty, owing, in the main, to the very feeble acidic properties of the substance. The inactive acid thus crystallises unchanged from solutions in the fairly powerful base, 1-tetrahydroquinoline, and can be extracted by appropriate neutral solvents from its mixtures with many of the optically active alkaloids. A clue to a successful mode of resolution was, however, ultimately derived from the observation that on

mixing aqueous solutions of brucine hydrochloride and sodium 1-methylcyclohexylidene-4-acetate a copious separation of an oil occurs; although this oily salt does not crystallise readily, the fact of its formation can be utilised for the isolation of the two enantiomorphously related acids.

As the result of a large amount of preliminary work, the following method was finally adopted for the resolution of the externally compensated acid. To a hot aqueous solution of two molecular proportions of externally compensated sodium 1-methylcyclohexylidene-4-acetate is added a hot aqueous solution of slightly less than one molecular proportion of brucine hydrochloride; during admixture, alcohol is added in just sufficient quantity to prevent the solution becoming turbid by the separation of an oily salt. On allowing the solution to cool slowly, an oil begins to separate, which, by persistent scratching with a glass rod, or better, by inoculation with crystalline salt obtained in a previous operation, may be caused to crystallise. In accordance with the experience of Pope and Peachey in connexion with the resolution of externally compensated bases (*Trans.*, 1899, **75**, 1066), it was to be expected that the crystalline salt which separated should be the least soluble of which the formation is possible in the system. The crystalline salt which separates under these conditions does, indeed, consist, in the main, of one product, namely, of brucine *l*-1-methylcyclohexylidene-4-acetate, so that the change can be expressed by the equation:



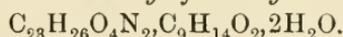
As will be pointed out later, however, a complicating factor is introduced, in that the two salts, *lBlA* and *lBdA*, behave as if they were partially isomorphous and form solid solutions.

The operation described above yields a crystalline separation, which has the composition of brucine *l*-1-methylcyclohexylidene-4-acetate, but which, on recrystallisation, is found to be by no means homogeneous; thus, in one case, on fractionally crystallising the separation obtained as described above from dilute alcohol in such a manner that the original separation was divided into five fractions, the consecutive fractions gave the following specific rotatory powers in 1 per cent. alcoholic solutions: $[\alpha]_D - 44.7^\circ$, $- 22.0^\circ$, $- 40.7^\circ$, $- 23.7^\circ$, and $- 33.6^\circ$.

The manner in which in these and a number of other trials the specific rotatory powers change from fraction to fraction indicates (1) that the original separation is a mixture of at least two substances, and (2) that the resolution of the mixture by recrystallisation does not follow the ordinary course; the separation is, in fact, complicated by the exhibition of behaviour somewhat similar to that observed with

mixtures of two substances which tend to form solid solutions, and readily yield supersaturated solutions. Since the two compounds present in the mixtures are presumably the *l*- and *d*-1-methylcyclohexylidene-4-acetates of *l*-brucine, it was, however, indicated by these results that some degree of separation could be effected by fractional crystallisation. Considerable quantities of the first separation of crystalline salt, obtained as above described, were therefore subjected to systematic fractional crystallisation from very dilute alcohol; the specific rotatory power of each fraction as it was separated was ascertained, and the numerous fractions were sorted into portions of approximately the same rotatory power. After a preliminary separation in this way into separate fractions of fairly uniform rotatory power, the systematic fractional crystallisation was repeated. As the final product of the prolonged application of this tedious process, a highly levorotatory salt was ultimately obtained, the rotatory power of which was unaltered by subsequent crystallisation. The material thus obtained gives all the ordinary indications of homogeneity, and separates from dilute alcoholic solution in elongated, colourless, rectangular prisms; it melts at 97—100° when dried in the air, and after expelling the water of crystallisation by heating at about 85°, commences to melt at 74°. As its properties appeared unaffected by further recrystallisation, it was regarded as the pure salt, *l*-brucine *l*-1-methylcyclohexylidene-4-acetate.

Brucine lævo-1-Methylcyclohexylidene-4-acetate,



A considerable quantity of salt answering to the above description having been accumulated, the whole was crystallised from dilute alcohol, and the following analyses and determinations of rotatory power made on the substance thus obtained:

0.3900, heated at 85°, lost 0.0242 H₂O. H₂O = 6.21.

0.0790, air-dried salt, gave 0.1902 CO₂ and 0.0522 H₂O.

Subtracting H₂O = 6.21; C = 73.00; H = 7.14.

C₃₂H₄₀O₆N₂, 2H₂O requires H₂O = 6.17; C = 70.02; H = 7.35 per cent.

For the determinations of the rotatory power, shown in the table below, the substance was made up to 20.05 c.c. with the solvent, and a 2-dm. tube employed in each case.

Substance	Solvent.	α_D .	$[\alpha]_D$.
gram.			
0.1553	Absolute alcohol	-0.90°	-58.1°
0.1570	" "	-0.91	-58.1
0.3983	" "	-1.98	-49.8
0.5680	" "	-2.66	-46.9
0.1683	Methylal	-1.32	-78.6
0.1458	Water	-0.56	-38.6

It thus appears that the specific rotatory power diminishes with increasing concentration in alcoholic solution, that the specific rotatory power is much higher in methylal solution, and that in water, in which alone the salt may be supposed to be practically completely dissociated, the specific rotatory power has the lowest value.

In view of the difficulty which attends the preparation of the salt characterised by the above constants, it was deemed advisable to subject the whole mass of material to further fractional crystallisation from dilute alcohol in order to make quite sure that its rotatory power had attained a constant value. It was therefore crystallised four times from absolute alcohol, and the following determination of the rotatory power made with the product :

0.1528 gram, made up to 20.05 c.c. with absolute alcohol, gave $\alpha_D - 0.89^\circ$ in a 2-dcm. tube ; whence $[\alpha]_D - 58.4^\circ$.

The material was then subjected to another and fifth crystallisation from the same solvent, and the product found to give the following results on determination of its rotatory power :

0.1494 gram, made up to 20.05 c.c. with absolute alcohol, gave $\alpha_D - 0.87^\circ$ in a 2-dcm. tube ; whence $[\alpha]_D - 58.4^\circ$.

Since in a 0.75 per cent. alcoholic solution the salt exhibited the specific rotatory power $[\alpha]_D - 58.1^\circ$, as quoted above, and after four and five recrystallisations the values $[\alpha]_D - 58.4^\circ$ and -58.4° were obtained, these being experimentally identical with the first, little doubt seemed possible concerning the homogeneity of the substance. The following work, however, showed that this conclusion is incorrect.

On decomposing a small portion of the salt by addition of hydrochloric acid, a sample of acid was obtained which melted at $51-52^\circ$, and gave the following result on determination of its rotatory power :

0.1253 gram, made up to 20.05 c.c. with absolute alcohol, gave $\alpha_D - 0.97^\circ$ in a 2-dcm. tube ; whence $[\alpha]_D - 77.6^\circ$.

The main quantity of the salt, which was in the form of stout, crystalline prisms, was next treated with hydrochloric acid, and the precipitated acid filtered ; associated with it, however, was some brucine hydrochloride, which could not be conveniently washed out with water. The whole mass was therefore warmed with sodium carbonate solution, and, after filtration, the acid was precipitated by hydrochloric acid, collected, washed, and dried. The acid thus obtained melted at $47.5-49.5^\circ$, and gave the following results on determination of its specific rotation :

0.1509 gram, made up to 20.05 c.c. with absolute alcohol, gave $\alpha_D - 1.10^\circ$ in a 2-dcm. tube ; whence $[\alpha]_D - 73.7^\circ$.

The residue left after warming the crude acid with sodium carbonate

solution as above described still contained acid ; this was extracted by successive treatments with hydrochloric acid and sodium carbonate solution, and melted very sharply at 52.5—53°. It gave the following results on determination of its rotatory power :

0.1459 gram, made up to 20.05 c.c. with absolute alcohol, gave $\alpha_D - 1.18^\circ$ in a 2-dcm. tube ; whence $[\alpha]_D - 81.1^\circ$.

It is thus seen that the salt which yields acid of specific rotatory power $[\alpha]_D - 77.6^\circ$ gives, when the acid is separated in two fractions as described above, samples having the specific rotatory powers, $[\alpha]_D - 73.7^\circ$ and $- 81.1^\circ$ respectively.

In view of the unsaturated character of the acid, it seemed advisable to ascertain whether the above variations in rotatory power were caused by optical inversion during the liberation of the acid from the brucine salt. A quantity of the acid having the specific rotatory power $[\alpha]_D - 73.7^\circ$ was therefore distilled in a current of steam ; the acid separated from the distillate was found to have the specific rotatory power $[\alpha]_D - 74.0^\circ$. A further portion of the same sample of acid was next heated for ten hours on the water-bath with excess of a 10 per cent. sodium carbonate solution ; during this treatment the solution became brown in colour, but the acid subsequently separated from it was found to exhibit the specific rotatory power of $[\alpha]_D - 71.9^\circ$. These results indicate that the optical activity of the acid is practically unaffected by somewhat drastic treatment, and show that the observed variations in rotatory power cannot be attributed to the occurrence of optical inversion.

The explanation of the anomalous behaviour of the brucine salt appears to be as follows. It is seen that prolonged fractional crystallisation is necessary in order to obtain a brucine salt of constant rotatory power, namely, $[\alpha]_D - 58.1^\circ$ in a 0.75 per cent. absolute alcoholic solution ; it is also observed that the salt is not homogeneous, because the two fractions of acid separated from it have the rotatory powers of $[\alpha]_D - 73.7^\circ$ and $- 81.1^\circ$ respectively. Taken together, these facts indicate that the salt of specific rotatory power $[\alpha]_D - 58.1^\circ$ is an equilibrium mixture of brucine *l*- and *d*-1-methylcyclohexylidene-4-acetates which is not resolvable by further fractional crystallisation from dilute alcohol under the conditions established ; the slowness with which the maximum rotatory power $[\alpha]_D - 58.4^\circ$ is attained during prolonged fractional crystallisation suggests that the two salts form solid solutions. This is also in accordance with the facts that both contain the same proportion of water of crystallisation, and that an approximately complete resolution of the externally compensated acid is not effected by the original crystallisation with one-half a molecular proportion of brucine. It was also observed that on decom-

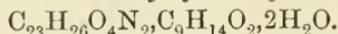
posing the salt of $[\alpha]_D - 58.4^\circ$, the first portion of acid separated has a lower rotatory power, $[\alpha]_D - 73.7^\circ$, than that which separated last, namely, $[\alpha]_D - 81.1^\circ$. This indicates that during the crystallisation of the brucine salt the salt with the lævo-acid first separated in a state of practical purity, and that subsequently the mixture of the two salts was deposited on the former as a kind of nucleus; since the crystals ultimately formed are quite massive, the outer layers were first decomposed by the hydrochloric acid, giving acid of the lower rotatory power, whilst the inner kernel was only decomposed by further treatment, and yielded acid of the higher rotatory power, $[\alpha]_D - 81.1^\circ$.

As no solvent other than dilute alcohol appears to be available for the fractional crystallisation of the brucine salt, it was useless, in view of the conclusions just derived, to attempt the further purification of the lævo-acid by the aid of the brucine salt. It is shown later, however, that the enantiomorphously related acid has the specific rotatory power $[\alpha]_D + 81.4^\circ$, so that the acid giving the value $[\alpha]_D - 81.1^\circ$ represents the pure *l*-1-methylcyclohexylidene-4-acetic acid.

The small difference in rotatory power between the pure lævo-acid of $[\alpha]_D - 81.1^\circ$ and that of $[\alpha]_D - 77.6^\circ$ yielded by the final crop of brucine salt, together with the large percentage of brucine contained in the brucine salt, rendered it certain that the specific rotatory powers observed with the brucine salt are practically the values appertaining to pure brucine *l*-1-methylcyclohexylidene-4-acetate. It seemed, however, desirable to check the numbers by preparing the latter salt from acid of $[\alpha]_D - 81.1^\circ$ by crystallising the components together from dilute alcohol. The pure salt was thus obtained in colourless, highly lustrous prisms having the properties already described in connexion with the slightly impure salt; the following determination of rotatory power was made:

0.1534 gram, made up to 20.05 c.c. with absolute alcohol, gave $\alpha_D - 0.89^\circ$ in a 2-dcm. tube; whence $[\alpha]_D - 58.2^\circ$.

Brucine dextro-1-Methylcyclohexylidene-4-acetate,



After the separation of the lævo-acid from the externally compensated substance in the manner described above, the mother liquors are treated with hydrochloric acid and the crude *d*-1-methylcyclohexylidene-acetic acid separated; it is convenient to mix with it acid recovered from the fractions of brucine salt of low rotatory power to which reference has been made above. In this way a pure mixture of the *d*- and *l*-acids can be obtained which has a specific rotatory power of about

+30°, and, although the salt formed by brucine with the lævo-acid is much less soluble than that formed with the dextro-acid, the isolation of pure brucine *d*-1-methylcyclohexylideneacetate is possible. The acid of specific rotatory power of about $[\alpha]_D + 30^\circ$ is dissolved in dilute alcohol with the addition of an equivalent quantity of pure brucine, and the salt formed subjected to prolonged fractional crystallisation from the same solvent. It is advisable so to adjust the concentrations of the solutions that crystallisation does not occur until the liquid is cold; under these conditions the salt of the lævo-acid tends to separate in massive crystals, whilst that of the dextro-acid crystallises in aggregates of light feathery needles. It is thus possible to effect a partial separation by mechanical means, but the final purification of the salt of the dextro-acid must be completed by fractional crystallisation alone. In one series of fractionations a sample of salt was first isolated which exhibited the specific rotatory power $[\alpha]_D - 22.6^\circ$, in alcoholic solution. Eight subsequent crystallisations of this material yielded samples having the specific rotatory powers of $[\alpha]_D - 18.7^\circ$, -16.9° , -16.3° , -13.5° , -14.6° , -12.8° , -10.4° , and -11.5° respectively. The apparently irregular fluctuations of the specific rotatory powers of the successive crystallisations were at first difficult to understand, but were ultimately traced to the fact that the rotatory power of the pure salt diminishes very rapidly with increase of concentration of the solution. The last three values quoted above thus refer to pure brucine *d*-1-methylcyclohexylidene-4-acetate.

This salt crystallises in colourless, feathery needles from dilute alcoholic solution, and melts at 85—86°; after drying at 70—80°, it begins to melt at 76°, but the melting point is very indefinite. This is possibly to be attributed to the substance melting as a mere mixture of the component base and acid:

0.5530, heated at 70—80°, lost 0.0403 H₂O. H₂O = 7.38.

0.0806, air-dried salt, gave 0.1929 CO₂ and 0.0560 H₂O.

Subtracting H₂O = 7.38; C = 70.53; H = 7.50.

C₃₂H₄₀O₆N₂·2H₂O requires H₂O = 6.17; C = 70.02; H = 7.35 per cent.

For the determinations of the rotatory power, quoted in the table below, the substance was made up to 20.05 c.c. with the solvent, and a 2-dcm. tube employed in each case.

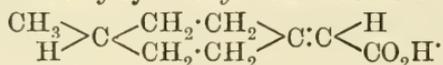
Substance. gram.	Solvent.	α_D .	$[\alpha]_D$.
0.2348	Absolute alcohol	-0.27°	-11.5°
0.4015	" "	-0.16	-3.9
0.5548	" "	-0.03	-1.4
1.0404	" "	+0.25	+2.4
0.1404	Methylal	-0.31	-22.1
0.1404	Water	-0.04	-2.9

It is interesting to note that the specific rotatory power of this salt

varies with the concentration and the solvent in just the same directions as that of the brucine salt of the lævo-acid. In alcoholic solutions the lævorotation diminishes with increasing concentration until in a 5 per cent. solution the salt is dextrorotatory, just as in the previous case the rotatory power in methylal solution is much higher than that in aqueous solutions.

The two brucine salts are converted into oils by the addition of small proportions of alcohol, acetone, or ethyl acetate, and are extremely soluble in these and most other organic solvents.

lævo-1-Methylcyclohexylidene-4-acetic Acid,



As already indicated above, the purest samples of this acid separated from its brucine salt are still contaminated with traces of the enantiomorphously related isomeride; it forms minute, colourless, crystalline scales, and cannot be conveniently crystallised from any of the ordinary solvents. It melts very sharply at 52.5—53°, whilst the externally compensated acid melts at 66°, and its melting point is depressed by the presence of the externally compensated substance. Specimens of mixtures of the two active acids exhibiting the specific rotatory powers $[\alpha]_D$ 12.3°, 24.2°, 52.8°, 73.7°, and 77.6° melt respectively at 61°, 42—57°, 43—44.5°, 47.5—49.5°, and 51—52°, so that the eutectic mixture has a considerably lower melting point than either the pure active or the pure externally compensated acid; the melting point curve of mixtures of the dextro- and lævo-acid is thus of the type depicted in Roozeboom's Fig. 7 (*Zeitsch. physikal. Chem.*, 1899, 28, 508), and indicates that the partially compensated substances melt as mixtures of optically active and racemic compounds.

The following determinations of rotatory power were made, the substance being made up to 20.05 c.c. with the solvent, and a 2-dcm. tube being employed in each case:

Substance. gram.	Solvent.	α_D .	$[\alpha]_D$.
0.1459	Absolute alcohol	-1.18°	-81.1°
0.1471	" "	-1.19	-81.1
0.3195	" "	-2.48	-77.8
0.1505	Methylal	-1.12	-74.6
0.1616	Ether	-1.20	-74.4

dextro-1-Methylcyclohexylidene-4-acetic Acid.

This acid, as stated above, has been obtained more easily and in a state of slightly higher purity than its enantiomorphously related isomeride. It has the same melting point of 52.5—53°, and its mixtures with the externally compensated acid behave just as do those of

the *laevo*-isomeride. The following determinations of rotatory power were made, the substance being made up to 20.05 c.c. with the solvent, and a 2-dm. tube being employed in each case :

Substance gram.	Solvent.	α_D .	$[\alpha]_D$.
0.1453	Absolute alcohol	+1.18°	+81.4°
0.2957	„	+2.30	+78.0
0.1487	Methylal	+1.12	+75.5
0.1478	Ether	+1.11	+75.3

The fact that the above values are slightly higher than the corresponding figures for the enantiomorphously related acid is the only indication yet obtained of the rather greater degree of purity of the preparations of the *dextro*-acid.

On dissolving equal quantities of the two optically active acids melting at 52.5—53° in light petroleum and evaporating to dryness, the racemic acid was obtained melting at 62.5—63°; that this melting point is rather lower than that of the pure externally compensated acid, namely, 66°, is obviously due to the mixture, which weighed only a few milligrams, containing a slight excess of one of the component acids.

The fact, established by the work detailed in the foregoing pages, that substances of enantiomorphous molecular configuration can now be prepared which exhibit optical activity in solution but yet contain no asymmetric carbon atom, suggests a mode of investigating intramolecular change which should have interesting results. The *d*- and *l*-methylcyclohexylidene-4-acetic acids owe their optical activity to the possession of an enantiomorphous molecular configuration of the most general kind, namely, one not associated with the presence of an asymmetric atom, and should be convertible into the potentially active 1-methylcyclohexeneacetic acid described by Marchwald and Meth, the optical activity of which is to be correlated with the presence of an asymmetric carbon atom. This conversion has not hitherto been described, and we have made a number of experiments in order to establish the conditions under which it occurs.

After heating 0.5 gram of racemic 1-methylcyclohexylidene-4-acetic acid with 10 c.c. of water and 2 grams of sodium hydroxide for five hours on the water-bath, or with 10 c.c. of aniline for three hours at 100°, the original acid can be recovered unchanged. Similarly, on boiling 1 gram of the sodium salt of the inactive acid with 2 grams of aniline hydrochloride and 20 c.c. of alcohol during two hours, the original acid is found to be unaltered. On boiling 0.5 gram of 1-methylcyclohexylidene-4-acetic acid with 20 c.c. of dilute sulphuric acid for three hours, 0.4 gram of the original acid was recovered unchanged, together with traces of Marckwald and Meth's 1-methylcyclohexene-4-acetic acid, melting at 41°. In another experiment,

0.5 gram of the inactive hexylidene acid melting at 64° was boiled for three hours with 10 c.c. of dilute sulphuric acid with the addition of sufficient alcohol for solution; on subsequent distillation with steam, a mixture of acid and ester was obtained, which, when hydrolysed, gave a mixture of the original acid with traces of the acid melting at 41° .

Acting on the indications thus obtained, 0.5 gram of racemic 1-methylcyclohexylidene-4-acetic acid was heated for three hours on the water-bath with a mixture of 4 grams of sulphuric acid, 1 gram of water, and 5 c.c. of alcohol; approximately equal quantities of acid and ester were isolated from the product. The acid consisted in the main of Marckwald and Meth's 1-methyl- Δ^3 -cyclohexene-4-acetic acid, melting at 41° , and the ester also yielded, on hydrolysis with alcoholic soda, a product consisting principally of the same acid.

A method is thus now available for the conversion of 1-methylcyclohexylidene-4-acetic acid into the isomeric 1-methyl- Δ^3 -cyclohexene-4-acetic acid. We are now studying this conversion, using the optically active hexylidene acids, together with several chemical changes of an additive character, as a result of which the enantiomorphous molecular configuration, containing no asymmetric atom, becomes converted into an enantiomorphous configuration of the well-known type which is associated with the presence of one or more asymmetric carbon atoms.

Our thanks are due to Dr. John Read for the care with which he has carried out much of the experimental work involved in the present paper.

CHEMICAL DEPARTMENT,
THE UNIVERSITY,
MANCHESTER.

THE CHEMICAL LABORATORY,
THE UNIVERSITY,
CAMBRIDGE.

THE UNIVERSITY,
GÖTTINGEN.

CXCIX.—*The Action of Ammonia on the Glycide Aryl Ethers. Part I. o-Tolyloxypropanolamines.*

By DAVID RUNCIMAN BOYD and HERBERT STANLEY KNOWLTON.

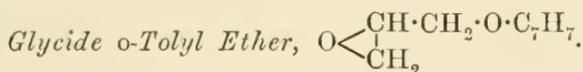
THE action of ammonia on substances of the type of ethylene oxide was originally studied by Wurtz (*Annalen*, 1860, **114**, 51). The reaction has since been reinvestigated by Knorr (*Ber.*, 1897, **30**, 909), who succeeded in isolating the primary, secondary, and tertiary ethanalamines in a pure condition.

Knorr has also studied the action of ammonia on glycide (*Ber.*,

1899, **32**, 750), and obtained γ -amino- $\alpha\beta$ -dihydroxypropane, along with secondary and tertiary bases which were not isolated.

The present paper contains an account of the action of ammonia on glycide *o*-tolyl ether. In this case, a primary, a secondary, and a tertiary base are readily isolated. Definite evidence has not so far been obtained with regard to the position which the amino-group takes up in the new molecule, but from analogy to the case of glycide, and in view of the results obtained by Krassusky in the case of the butylene oxides (*Compt. rend.*, 1908, **146**, 236), it appears probable that the primary base is β -amino- β' -*o*-tolyl-*oxy*-isopropyl alcohol, $C_7H_7 \cdot O \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot NH_2$.

EXPERIMENTAL.



o-Cresol (80 grams) was dissolved in about 500 c.c. of water containing excess of sodium hydroxide, and rather more than the theoretical quantity of epichlorohydrin was added to the cold solution. After the mixture had been kept for about four days, with occasional stirring, the heavy oil which had separated was extracted with ether, the ethereal solution dried and evaporated, and the oil which remained was fractionated under diminished pressure.

In this way, the glycide ether was obtained as a colourless oil, boiling at $136^\circ/17$ mm., and, with slight decomposition, at 248° under atmospheric pressure. The yield was about 28 grams.

The glycide *o*-tolyl ether so prepared still contained traces of chlorine. It was therefore warmed on the water-bath with solid sodium hydroxide, and again fractionated under diminished pressure (compare Boyd and Marle, *Trans.*, 1908, **93**, 840). The fraction analysed boiled at $134.5^\circ/14$ mm.:

0.2813 gave 0.7523 CO_2 and 0.1872 H_2O . C=72.94; H=7.46.

$C_{10}H_{12}O_2$ requires C=73.12; H=7.38 per cent.

Action of Ammonia on Glycide o-Tolyl Ether.

If glycide *o*-tolyl ether is kept for some days in contact with a concentrated aqueous solution of ammonia, it changes into a crystalline mass, which consists chiefly of the tertiary base, trihydroxytri-*o*-tolyl-*oxy*tripropylamine, whilst the primary base is present in the aqueous solution.

A more convenient and rapid method of bringing about the reaction consists in adding to the mixture of glycide *o*-tolyl ether

and ammonia a sufficient quantity of alcohol to give a clear solution. After about forty-eight hours at the ordinary temperature, the glycide ether is completely transformed into a mixture of primary, secondary, and tertiary bases. The end of the reaction can be recognised by pouring a few drops of the aqueous alcoholic solution into water. If the reaction is finished, the oily precipitate which is at first produced will be found to solidify rapidly. The mixture is then heated on a water-bath to expel the alcohol and ammonia, water being added occasionally to prevent the solution becoming too concentrated.

In the course of the evaporation, an oil separates which solidifies on cooling. The solid is collected and used for the preparation of the secondary and tertiary bases. The filtrate is then evaporated on the water-bath to a small volume. The syrupy residue left after most of the water has been expelled consists of a mixture of the primary base and its carbonate, the latter being formed during the process of evaporation.

In one experiment, 18.1 grams of glycide *o*-tolyl ether were mixed with 170 c.c. of concentrated aqueous ammonia and an equal volume of alcohol. As a result, 16.5 grams of the hydrochloride of the primary base (equal to about 14 grams of free base) were obtained, 1.4 grams of the secondary base, and about 3 grams of tertiary base.

β-Amino-β'-*o*-tolylloxypipropyl Alcohol, $C_{10}H_{13}O_2 \cdot NH_2$.

The *hydrochloride* of this base is obtained as a crystalline precipitate on adding concentrated hydrochloric acid to the mixture of free base and carbonate prepared as above described. It can be recrystallised by dissolving in alcohol, and adding about two volumes of ether. It then separates in colourless plates, which soften at 131°, but do not melt completely until 254°. Repeated fractional crystallisation does not alter this melting point:

0.2750 gave 15.6 c.c. N_2 (moist) at 20° and 750 mm. $N = 6.40$.

$C_{10}H_{15}O_2N \cdot HCl$ requires $N = 6.44$ per cent.

The salt is extremely readily soluble in cold water, giving a neutral solution. It is precipitated from a concentrated aqueous solution on addition of hydrochloric acid.

The free base was prepared by treating a concentrated aqueous solution of the hydrochloride with excess of sodium hydroxide. The oil which separated was extracted with ether, and the ethereal solution dried, evaporated, and the residue fractionated under diminished pressure, when a colourless, viscous oil, boiling at 177°/11 mm., was obtained. This oil crystallised after some hours

as a mass of plates. The crystals, after washing with a little dry ether, softened at 53°, and melted at 58—60°:

0·2107 gave 0·5140 CO₂ and 0·1592 H₂O. C = 66·53; H = 8·47.

0·0860 „ 5·9 c.c. N₂ (moist) at 21° and 753 mm. N = 7·74.

C₁₀H₁₅O₂N requires C = 66·24; H = 8·36; N = 7·73 per cent.

β-Amino-β'-o-tolyloxyisopropyl alcohol dissolves moderately easily in cold water, giving a solution with a strongly alkaline reaction to litmus. It is readily soluble in alcohol, and rather less so in ether. The solid base deliquesces rapidly in moist air, and absorbs carbon dioxide readily.

The *platinichloride* separates in yellow needles on adding platinic chloride to a concentrated aqueous solution of the hydrochloride. It melts and decomposes at 203°:

0·3060 gave 0·0760 Pt. Pt = 24·84.

(C₁₀H₁₅O₂N)₂·H₂PtCl₆ requires Pt = 25·25 per cent.

The *oxalate*, (C₁₀H₁₅O₂N)₂·H₂C₂O₄, is obtained as a crystalline precipitate on adding a solution of ammonium oxalate to a concentrated aqueous solution of the hydrochloride. On recrystallisation from hot dilute alcohol, it forms shining leaflets, which decompose rapidly at 200°:

0·1960 gave 11·2 c.c. N₂ (moist) at 21° and 744 mm. N = 6·36.

C₂₂H₃₂O₈N₂ requires N = 6·19 per cent.

The *benzoate*, C₁₀H₁₅O₂N·C₇H₆O₂, separates as an oil, which soon becomes crystalline, on mixing aqueous solutions of equivalent proportions of the hydrochloride and sodium benzoate. On recrystallisation from moist ethyl acetate, it forms clusters of prismatic crystals, which soften at 131° and melt at 132—133°:

0·1940 gave 7·8 c.c. N₂ (moist) at 20° and 743 mm. N = 4·50.

C₁₇H₂₁O₄N requires N = 4·62 per cent.

The *benzoyl* derivative, C₁₀H₁₃O₂·NHBz, prepared by the Schotten-Baumann method and crystallised from ethyl acetate, formed prismatic needles, melting at 114·5—115·5°:

0·2346 gave 11 c.c. N₂ (moist) at 20° and 743 mm. N = 5·24.

C₁₇H₁₉O₃N requires N = 4·91 per cent.

Dihydroxydi-o-tolyloxydipropylamine, (C₁₀H₁₃O₂)₂NH.

The mixture of secondary and tertiary bases obtained as above described was treated with cold ether. A portion remained undissolved, and was collected, washed with ether, and crystallised from hot ethyl acetate. On recrystallisation from the same solvent, it formed rosettes of needles, melting at 117·5°:

0.1120 gave 0.2856 CO₂ and 0.0776 H₂O. C=69.54; H=7.77.

0.2911 ,, 10.5 c.c. N₂ (moist) at 17° and 751 mm. N=4.14.

C₂₀H₂₇O₄N requires C=69.51; H=7.90; N=4.06 per cent.

The base dissolves readily in alcohol, giving a solution with an alkaline reaction. It is insoluble in water, and only very sparingly soluble in cold ether.

*Trihydroxytri-*o*-tolylxytripropylamine*, (C₁₀H₁₃O₂)₃N.

On evaporation of the ethereal solution, which has been filtered from the insoluble secondary base, the tertiary base is left. It can also be prepared by keeping glycidic *o*-tolyl ether for some days in contact with concentrated aqueous ammonia. The glycidic ether changes gradually into a cake of white crystals, consisting chiefly of the tertiary base. It was recrystallised by dissolving in ethyl alcohol, adding a little water to the hot solution, and allowing to cool slowly. It separated in clusters of leaflets, melting at 83—84°:

0.2095 gave 0.5409 CO₂ and 0.1484 H₂O. C=70.41; H=7.94.

0.4803 ,, 12.2 c.c. N₂ (moist) at 19.5° and 751 mm. N=2.84.

C₃₀H₃₉O₆N requires C=70.67; H=7.73; N=2.75 per cent.

The base dissolves readily in alcohol or ether. The alcoholic solution is neutral to litmus.

The *hydrochloride* is obtained on adding concentrated hydrochloric acid to a hot alcoholic solution of the base. The salt deposits, on cooling, in crystals, melting at 134—135°:

0.3180 gave 0.0804 AgCl. Cl=6.26.

C₃₀H₃₉O₆N.HCl requires Cl=6.48 per cent.

The *platinichloride* is obtained on adding platinic chloride to a warm concentrated solution of the hydrochloride in alcohol containing hydrochloric acid. It melts at 141°:

0.3602 gave 0.0497 Pt. Pt=13.79.

(C₃₀H₃₉O₆N)₂.H₂PtCl₆ requires Pt=13.65 per cent.

*Trihydroxytri-*o*-tolylxytripropylamine Oxide*, (C₁₀H₁₃O₂)₃N.O.

This substance was prepared by adding to a solution of one gram of trihydroxytri-*o*-tolylxytripropylamine in 10 c.c. of glacial acetic acid about 5 c.c. of 30 per cent. hydrogen peroxide, and warming on a water-bath for about half an hour at 70—80°.

The mixture was then cooled and poured into water. Excess of sodium hydroxide was added, and the whole shaken with ether. From the ethereal solution so obtained, crystals of the oxide separated almost immediately. After washing with ether, the

substance was dissolved in hot benzene, from which, on cooling, it separated in minute prisms.

After recrystallisation it melted at 151° :

0.1915 gave 0.4801 CO_2 and 0.1268 H_2O . C = 68.38; H = 7.42.

0.2878 ,, 7.1 c.c. N_2 (moist) at 8° and 739 mm. N = 2.89.

$\text{C}_{30}\text{H}_{39}\text{O}_7\text{N}$ requires C = 68.51; H = 7.50; N = 2.67 per cent.

CHEMICAL DEPARTMENT,
HARTLEY UNIVERSITY COLLEGE.

CC.—*The Action of Potassium Hydroxide on Epichlorohydrin in Presence of Monohydric Phenols.*

By DAVID RUNCIMAN BOYD and ERNEST ROBERT MARLE.

UNDER the above title, Zunino has recently published a paper (*Atti R. Accad. Lincei*, 1909, [v], **18**, i, 254), in which certain of the diaryl ethers of glycerol are described.

The author is apparently unaware of the fact that three of the ethers which he describes were prepared some years ago, the diphenyl ether, $\text{OH}\cdot\text{CH}(\text{CH}_2\cdot\text{OPh})_2$, by Rössing (*Ber.*, 1886, **19**, 63) and Lindeman (*Ber.*, 1891, **24**, 2147), and the di-*o*-tolyl and di-*m*-tolyl ethers by one of us (Boyd, *Trans.*, 1903, **83**, 1137 and 1139). This is the more extraordinary since the question of the constitution of these substances was discussed by us less than a year ago (*Trans.*, 1908, **93**, 838).

Moreover, the statements made by Zunino with regard to the properties of these substances are incorrect.

The diphenyl ether is described as a liquid boiling at $287\text{--}288^{\circ}$, whereas it is really a crystalline solid melting at $81\text{--}82^{\circ}$, and boiling, with considerable decomposition, at the ordinary pressure at $343\text{--}345^{\circ}$ (uncorr.).

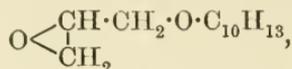
The di-*o*-tolyl ether is described as a liquid boiling at 296° , whilst, as a matter of fact, it is a solid melting at $36\text{--}37^{\circ}$, and boiling at $226^{\circ}/13$ mm.

The di-*m*-tolyl ether is described as boiling at $253\text{--}254^{\circ}$, whilst we have found it to boil at $232^{\circ}/13$ mm., and, with considerable decomposition, at 363° under atmospheric pressure.

Two other ethers are described by Zunino, namely, a dithymyl and a dicarvacryl ether, which have not hitherto been prepared. The boiling points assigned to the compounds, however (for the dithymyl ether 215° , for dicarvacryl ether 245°), appeared to us

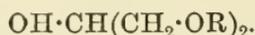
so improbable that we thought it desirable to investigate the action of epichlorohydrin on thymol in the presence of alkalis.

As a result, we have obtained glycide thymyl ether,



and glycerol dithymyl ether, $\text{OH} \cdot \text{CH}(\text{CH}_2 \cdot \text{O} \cdot \text{C}_{10}\text{H}_{13})_2$. The former substance is an oil boiling at $158^\circ/16$ mm., and the latter is a crystalline solid, melting at $41\frac{1}{2}$ — 42° , and boiling at $270^\circ/28$ mm.

In Zunino's paper, no reference is made to the fact that by the action of epichlorohydrin on phenols in the presence of alkalis two different products may be obtained, namely, (1) the glycide aryl ether, $\text{O} \begin{array}{l} \text{CH} \cdot \text{CH}_2 \cdot \text{OR}, \\ | \\ \text{CH}_2 \end{array}$, and (2) the glycerol diaryl ether,



We were at first inclined to suppose that the substances obtained by Zunino were really the glycide aryl ethers. However, a comparison of the boiling points recorded with those of the glycide aryl ethers in question shows a wide discrepancy (40 — 50°), and we can only account for his data by supposing that he was dealing with mixtures of the two substances.

EXPERIMENTAL.

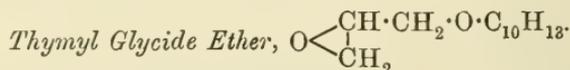
Glycerol Dithymyl Ether, $\text{OH} \cdot \text{CH}(\text{CH}_2 \cdot \text{O} \cdot \text{C}_{10}\text{H}_{13})_2$.

This substance was prepared by the method previously described for the diphenyl ether (Trans., 1908, **93**, 840). On pouring the reaction mixture into water, an oil separated. This was extracted with ether, and, after removal of the ether, fractionated under diminished pressure. In this way, a colourless, dense, very viscous oil was obtained, boiling at $270^\circ/28$ mm. On keeping, it solidified to a crystalline mass, melting at $41\frac{1}{2}$ — 42° :

(1) 0.2306 gave 0.6580 CO_2 and 0.1867 H_2O . C = 77.82; H = 9.06.

(2) 0.1297 „ 0.3696 CO_2 „ 0.1069 H_2O . C = 77.70; H = 9.22.

$\text{C}_{23}\text{H}_{32}\text{O}_3$ requires C = 77.52; H = 8.98 per cent.



Twenty grams of sodium hydroxide (2 mols.), 35 grams of thymol (rather less than 1 mol.), and 23 grams of epichlorohydrin (1 mol.) were used. The sodium hydroxide was dissolved in 100 c.c. of water, and the thymol added. Epichlorohydrin dissolves completely in this solution, forming a slightly yellow liquid, from which an oil separates on keeping, and rises to the surface. After

four days, the oil was separated, warmed for half an hour with powdered sodium hydroxide on the water-bath, and then dissolved in ether. The ethereal solution was washed with water, dried, and the oil left after evaporation of the ether was fractionated under diminished pressure. A colourless, fairly mobile oil, with a faint odour, was obtained, which boiled at $158^{\circ}/16$ mm. The residue, about half of the original oil, consisted mainly of glycerol dithymyl ether:

- (1) 0.2666 gave 0.7440 CO_2 and 0.2114 H_2O . C = 76.10; H = 8.87.
 (2) 0.3069 „ 0.8528 CO_2 „ 0.2403 H_2O . C = 75.77; H = 8.77.
 $\text{C}_{13}\text{H}_{18}\text{O}_2$ requires C = 75.73; H = 8.74 per cent.

CHEMICAL DEPARTMENT,
 HARTLEY UNIVERSITY COLLEGE.

CCl.—*The Constitution of Hydroxyazo-compounds.* *Part II.*

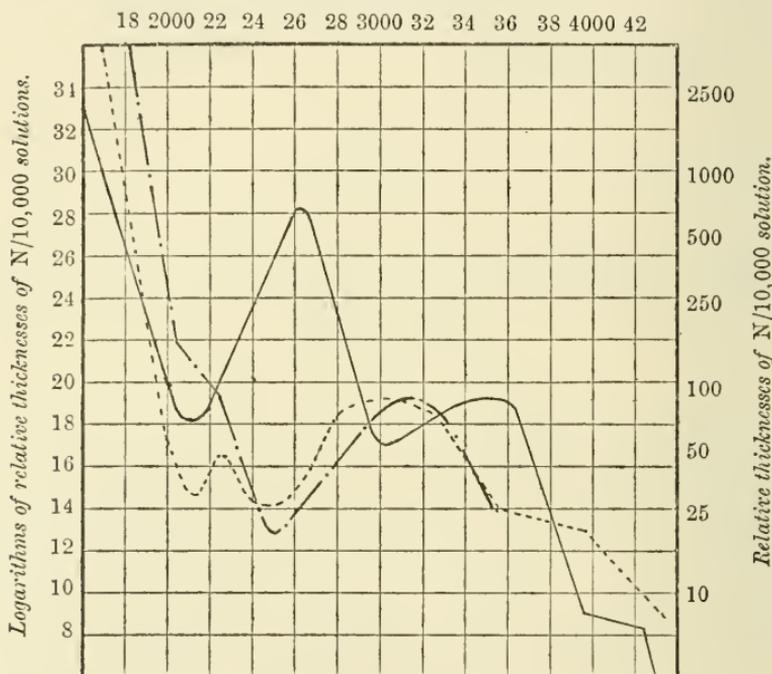
By WILLIAM BRADSHAW TUCK.

IN a previous communication (Trans., 1907, **91**, 449) the results of a spectroscopic examination of simple hydroxy-derivatives of azobenzene were given, and the absorption curves obtained were compared with those of azobenzene and *p*-benzoquinonebenzoylphenylhydrazone. The *p*-hydroxyazo-compounds, their ethers and acyl derivatives, and the ethers of *o*-hydroxyazo-compounds showed absorption curves very closely resembling the curve for azobenzene. The only difference was that the persistence or depth of the band in the colour region varied with the group attached to the azobenzene nucleus. The head of the colour band belonging to the above-mentioned substances always appeared at 250 mm. of *N*/10,000 solution. On the other hand, the colour band of the *o*-hydroxyazo-compounds and their acyl derivatives always appeared at about 25 mm. of *N*/10,000 solution. Thus the absorption curves could be divided into two classes, the one having the head of its isorropesis band at ten times the dilution at which the colour band of the second class appeared. Since the difference between benzene-azophenol benzoate and the isomeric *p*-benzoquinonebenzoylphenylhydrazone was of a similar nature, the conclusion was drawn that the two types of absorption curves were characteristic of two different constitutions, namely, the hydroxyazo- and the quinonehydrazone structures.

This conclusion was criticised by Auwers (*Annalen*, 1908, **360**, 11) and by C. Smith and Mitchell (*Trans.*, 1908, **93**, 842), both of whom considered that the difference between the two sets of curves was not sufficient to justify it. Both authors neglect the fact that the ratio of the dilutions at which the colour bands of any ortho-compound and its ether appear (roughly 1:10) is of the same order as that obtained from the absorption curves of the

FIG. 1.

Oscillation frequencies.



Full curve: α -Naphthaquinonephenylmethylhydrazone in alcohol.
 Dotted ,, Benzeneazo- α -naphthol
 Dot and dash curve: Benzeneazo- α -naphthol ethyl ether ,,

isomeric benzeneazophenol benzoate and *p*-benzoquinonebenzoylphenylhydrazone.

In order to obtain further evidence, the absorption spectra of the benzeneazonaphthols were investigated. It seemed probable that results of importance would be obtained, since MacPherson (*Amer. Chem. J.*, 1899, **22**, 364) had described the preparation of both α - and β -naphthaquinonephenylmethylhydrazone. The latter compound would give definitely the curve for a hydrazone of an *o*-quinone. MacPherson obtained the substance by the action of phenylmethylhydrazine on β -naphthaquinone in fairly dilute solu-

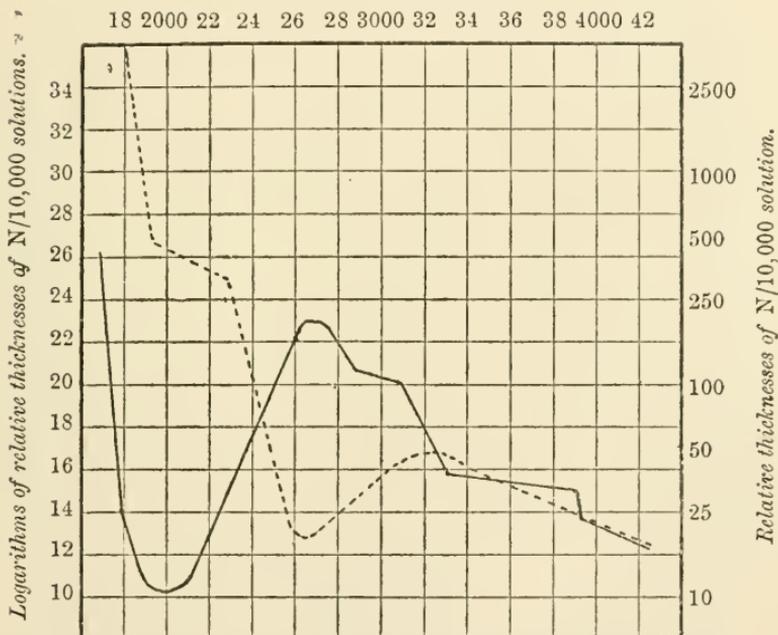
tion, in a 2 per cent. yield. Unfortunately, I was unable to prepare the substance by the method given, and a series of attempts to obtain it all resulted in failure.

The substances of this group which were examined were α -naphthaquinonephenylmethylhydrazone, benzeneazo- α -naphthol, its ether and acetyl compound, benzeneazo- β -naphthol and its acetate, and β -naphthaquinonephenylhydrazone and its acetyl derivative. The curves are given in Figs. 1, 2, 3, and 4.

The absorption spectra of these compounds show no relation to

FIG. 2.

Oscillation frequencies.



Full curve : Benzeneazo- α -naphthol in alcoholic sodium chloride.
Dotted ,, Benzeneazo- α -naphthyl acetate in alcohol.

that of azobenzene, or to those of previously recorded hydroxyazo-compounds. This was quite unexpected, and no reason for it could be seen from previous work. When, however, as will be described later, the effect of various substituting groups on azobenzene was studied, the explanation was obtained.

An examination of Fig. 1 shows that α -naphthaquinonephenylhydrazone and benzeneazo- α -naphthol ethyl ether, although having different constitutions, exhibit absorption spectra which are so nearly alike that it is not obvious to which class benzeneazo-

α -naphthol itself belongs. Since, therefore, the problem is not easy in the case of the para-compounds, the ortho-compounds could,

FIG. 3.

Full curve: *Benzeneazo- β -naphthol in alcohol.*
 Dotted " " " " *alcoholic sodium ethoxide.*
 Dot and dash curve: *Benzeneazo- β -naphthyl acetate in alcohol.*

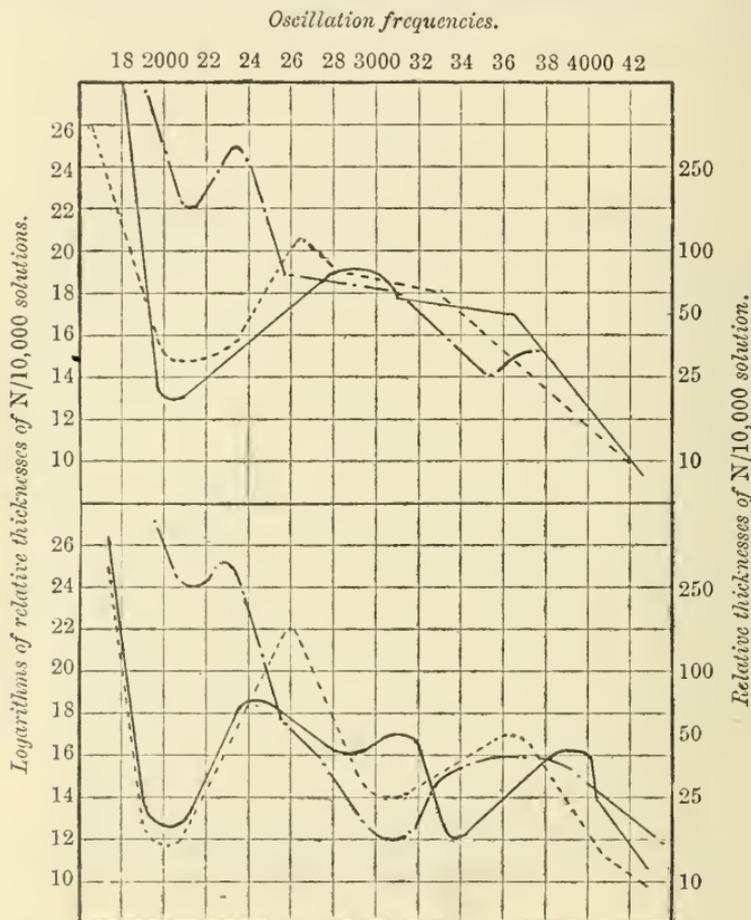


FIG. 4.

Full curve: *β -Naphthaquinonephenylhydrazone in alcohol.*
 Dotted " " " " *alcoholic sodium ethoxide.*
 Dot and dash curve: *Acetyl- β -naphthaquinonephenylhydrazone in alcohol.*

still less, be expected to yield results of value, as the absorption curve for the *o*-quinonehydrazone form cannot be obtained.

A fresh line of research was then undertaken, and compounds were examined which contained a hydroxy- or methoxy-group in

the ortho-position with respect to a group containing a double bond similarly situated to that in benzeneazo-*p*-cresetole (I) :

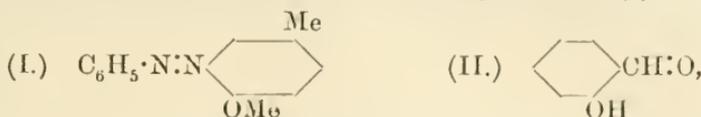


FIG. 5.

Full curve : *Salicylaldehyde in alcohol.*
 Dotted " " " " *alcoholic NaOEt.*
 Dot and dash curve : *o-Methoxybenzaldehyde in alcohol.*

Oscillation frequencies.

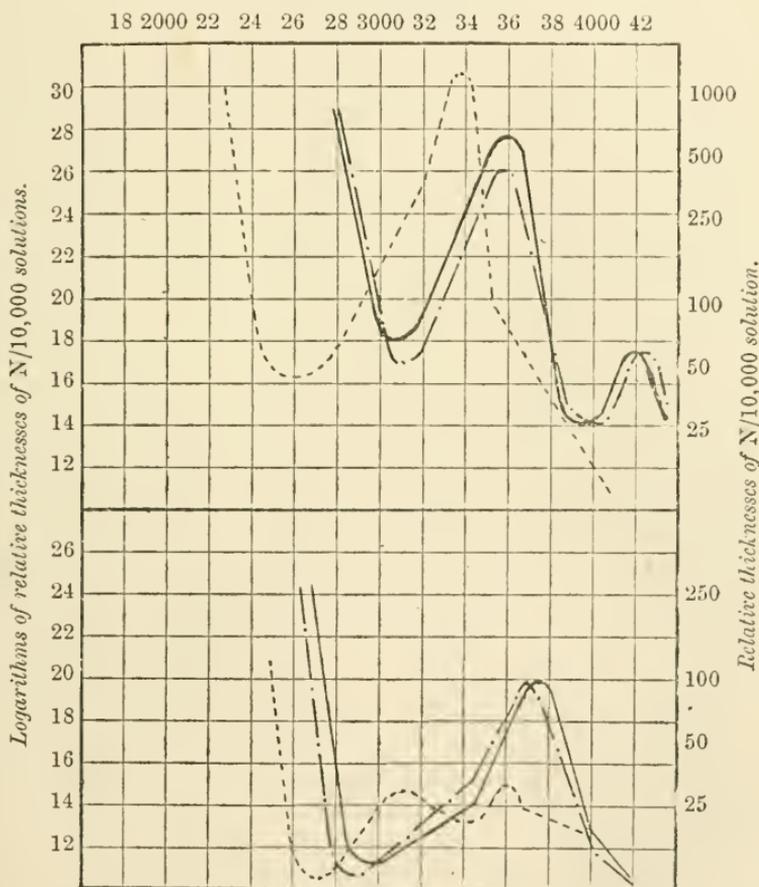


FIG. 6.

Full curve : *Salicylaldehydephenylmethylhydrazone in alcohol.*
 Dotted " " " " *alcoholic NaOEt.*
 Dot and dash curve : *o-Methoxybenzaldehydephenylmethylhydrazone in alcohol.*

The substances used were salicylaldehyde (II) and its methyl ether, and the phenylmethylhydrazones of both compounds.

For comparison, the corresponding derivatives of *p*-hydroxybenzaldehyde were examined. The phenylmethylhydrazones were used in preference to the phenylhydrazones, since many of the latter

FIG. 7.

Full curve: *p*-Hydroxybenzaldehyde in alcohol.
Dotted " " " alcoholic NaOEt.
Dot and dash curve: Anisaldehyde in alcohol.

Oscillation frequencies.

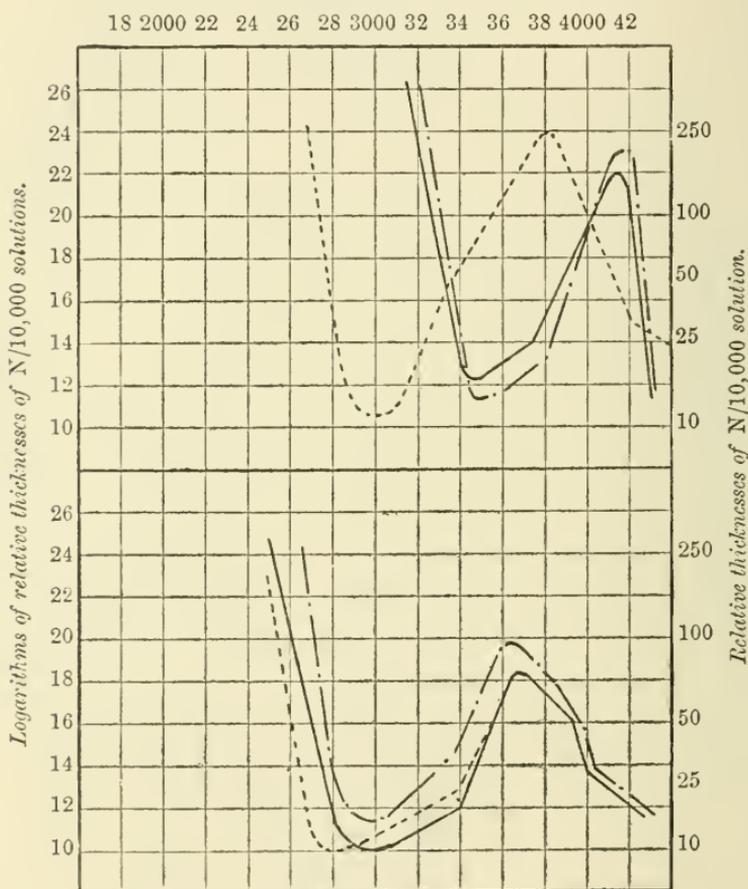


FIG. 8.

Full curve: *p*-Hydroxybenzaldehydephenylmethylhydrazone in alcohol.
Dotted " " " " " alcoholic NaOEt.
Dot and dash curve: Anisaldehydephenylmethylhydrazone in alcohol.

undergo isomeric change (Baly and Tuck, Trans., 1906, **89**, 892). The curves are given in Figs. 5, 6, 7, and 8. In every case the corresponding hydroxy- and methoxy-compounds show absorption

spectra which are practically identical. This is in agreement with the observations in the case of *p*-hydroxyazo-compounds and their ethers. When the close relation between these hydroxy- and methoxy-compounds is compared with the enormous difference between an *o*-hydroxyazo-compound and its ether, it is obvious that the two latter compounds cannot have the same constitution, or, in other words, the parent substance must be a quinone-hydrazone.

The influence of sodium ethoxide on the absorption spectra of this compound has also been studied, and very considerable light is thrown by this means on the constitution of substituted azo-compounds. In every case the characteristic band of the hydroxy-compound is shifted towards the red, and as the band is unaltered in shape it is extremely improbable that this denotes a change of constitution. This shift towards the red end of the spectrum has been observed in the case of phenol itself (Baly and Ewbank, *Trans.*, 1905, **87**, 1347). Reference to the absorption curves (Figs. 5 and 7) shows that in the case of *p*-hydroxybenzaldehyde, sodium ethoxide causes the band to shift almost to the edge of the visible region. In the case of salicylaldehyde, the shift is still greater; the absorption band is now in the blue region, the substance being therefore yellow in colour.

It has already been shown that the difference between the absorption spectra of the *o*-hydroxyazo-compounds and their ethers is practically the same as that between the curves obtained for a *p*-hydroxyazo-compound and the isomeric quinonehydrazone (Tuck, *loc. cit.*), and in the present paper it is shown that they are different from all other hydroxy-compounds in that the absorption spectra of their ethers are considerably different from those of the parent compounds.

An effort was then made to obtain a substance which, whilst undoubtedly an azo-compound, would show an absorption curve similar to those of *o*-hydroxyazo-compounds and their acyl derivatives. It was shown in a previous paper (Tuck, *loc. cit.*) that the colour band of azobenzene was modified by substituting groups, in a similar manner to the effect produced by the same groups on the absorption spectrum of benzene. Thus, it was shown that an acetoxy-group caused a smaller change than a hydroxy-group, that is, the group with the smaller residual affinity produced less change than one of greater residual affinity.

Although no group could be found which produced an absorption spectrum similar to that of the *o*-hydroxyazo-compounds, still the work resulted in the discovery of a reason for the isorropesis bands of the sodium salts of the *p*-hydroxyazo-compounds, and for the

difference between the absorption spectra of benzeneazo- α -naphthol, together with its derivatives, and azobenzene.

In benzeneazophenol, the absorption spectrum consists of a "step out" or limit of an absorption band in the visible region, with

FIG. 9.

Full curve: *Azophenetole in alcohol.*
 Dotted " " " " *alcoholic NaOEt.*
 Dot and dash curve: *p-Methoxybenzeneazophenol in alcohol.*
Oscillation frequencies.

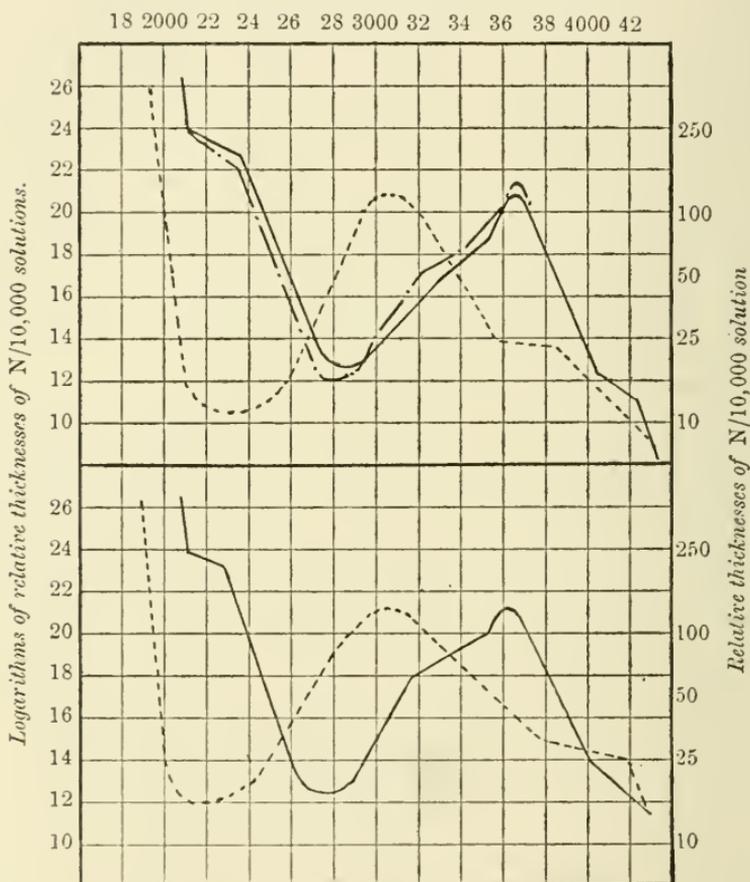


FIG. 10.

Full curve: *Azophenol in alcohol.*
 Dotted " " " " *alcoholic NaOEt.*

a large band in the ultraviolet. If the curve for azophenetole (Fig. 9) is examined, it is seen that the general appearance of the curve is that of benzeneazophenol, but the sudden extension in the visible region is slightly smaller, and also the ultraviolet band has

shifted towards the red end of the spectrum. In *p*-methoxybenzeneazophenol, this phenomenon is slightly more marked, and in azophenol the alteration is still greater. Thus, since the residual affinity of a hydroxyl group is slightly greater than that of an ethoxy-group, the residual affinity is increased progressively when passing along the series, benzeneazophenol, azophenetole, *p*-methoxybenzeneazophenol, and azophenol. The change of absorption is proportional to the residual affinity attached to the azobenzene nucleus.

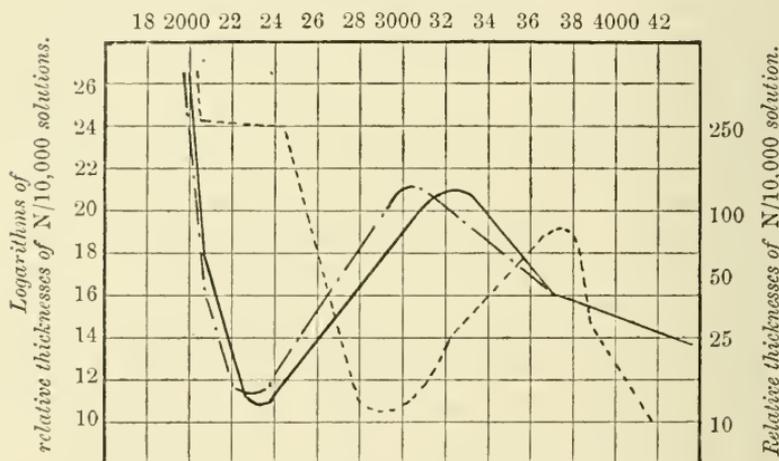
If now we turn to the absorption spectra of amino- and dimethyl-amino-azobenzene, we find that, whilst they are practically identical, the colour band of azobenzene has disappeared, and the ultraviolet band has been shifted right into the visible region. The band in these two compounds is the same as that which the sodium salts of *p*-hydroxyazo-compounds also show. This means that the effect of the substitution of an amino-group in azobenzene is identical with that produced by the substitution of an $\cdot\text{ONa}$ -group. From this we may conclude that so far as their effective residual affinity is concerned, the amino- and $\cdot\text{ONa}$ -groups are identical. This is confirmed by a reference to the absorption curves of aniline (Baly and Collie, *Trans.*, 1905, **87**, 1332) and sodium phenoxide (Baly and Ewbank, *loc. cit.*), which show absorption bands that are exactly the same. Now, Baly and Ewbank showed that the characteristic band of phenol was shifted towards the red by the addition of sodium ethoxide. In the earlier part of this paper, it is shown that an unsaturated group, namely, an aldehydic group, attached to a phenol nucleus produces a similar effect. Thus *p*-hydroxybenzaldehyde exhibits the phenol band considerably shifted towards the red end of the spectrum. This shift can be accentuated by the addition of sodium ethoxide. This renders it probable that the bands of aminoazobenzene and the sodium salt of benzeneazophenol are merely those of aniline and sodium phenoxide respectively, shifted into the visible region by conjugation with the unsaturated group, $\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_5$. Since the absorption spectra of aniline and sodium phenoxide are identical, the bands of aminoazobenzene and the sodium salt of benzeneazophenol are the same.

In acetanilide, the effect of the acetyl group on the absorption spectrum of aniline is entirely to change its character, probably owing to the residual affinity of the nitrogen atom being conjugated with that of the acetyl group. If, then, the hypothesis as regards the absorption spectrum of aminoazobenzene is correct, then acetyl-aminoazobenzene should show a type of absorption closely related to that of azobenzene. A reference to the curve, Fig. 11, shows that this is so.

From the curves given, it is seen that the absorption spectra of azo-compounds show a gradual change from that of azobenzene itself, the amount of change being proportional to the residual affinity attached to the azo-nucleus. The limit of change is apparently reached in the case of aminoazobenzene, since the absorption spectrum of *p*-aminobenzeneazophenol (Hewitt, *Trans.*, 1908, **95**, 1292) is practically identical with that of aminoazobenzene.

Benzeneazo- α -naphthol is a compound which shows the same type of absorption spectrum as aminoazobenzene, the band in the visible region being the α -naphthol band shifted towards the longer wavelengths by conjugation with the group $\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_5$.

FIG. 11.

Oscillation frequencies.Full curve: *Aminoazobenzene in alcohol.*Dotted „ *Acetylaminoazobenzene in alcohol.*Dot and dash curve: *Dimethylaminoazobenzene in alcohol.*

The absorption spectra of compounds known to be azo-compounds fall between the extreme limits shown in the case of azobenzene and aminoazobenzene. It has been pointed out that by suitably substituting groups in the azobenzene nucleus, absorption spectra anywhere between these limits can be obtained. The absorption spectra of *o*-hydroxyazo-compounds cannot be obtained in this way, and the fact that they do not fall between the two limits found renders it extremely improbable that these ortho-compounds are really derivatives of azobenzene.

In conclusion, the results obtained show that, whilst in general the curves for *o*-hydroxy-compounds and their ethers are practically

identical, those of the so-called *o*-hydroxyazo-compounds and their ethers are comparatively widely different. Again, the curves for the parent *o*-hydroxyazo-compounds do not show absorption spectra within the limits obtained for undoubted azo-compounds. These results, together with the resemblance between *o*-hydroxyazo-compounds and *p*-benzoquinonebenzoylphenylhydrazone, lead to the conclusion that the ortho-compounds are really quinonehydrazones.

SPECTROSCOPIC LABORATORY,
UNIVERSITY COLLEGE, LONDON.

CCII.—*The Iodination of Phenols and the Iodometric Estimation of, and Action of Reducing Agents on, Tannic Acid.*

By WALTER M. GARDNER, M.Sc., and HERBERT H. HODGSON, M.A., B.Sc., Ph.D.

THE chief object of the work described in this paper* was to devise a rapid quantitative and absolute method for the estimation of tannic and gallic acids.

Action of Reducing Agents on Tannic and Gallic Acids.

From the known constitution of gallic acid, and from the formulæ ascribed to tannic acid, a quantitative yield of benzoic acid might be expected on reduction. Böttinger (*Annalen*, 1890, **258**, 252), acting with metallic sodium on a solution of tannic or gallic acid in absolute alcohol, obtained no reduction product, but Guignet (*Compt. rend.*, 1891, **113**, 130) found that both tannic and gallic acids yield benzoic acid when treated with zinc dust in acid or alkaline solution.

After repeating these experiments, tannic acid was submitted to the action of reducing agents under various conditions, and it was found that, whilst little or no reaction takes place in neutral or acid solution, tannic acid is very reactive towards alkaline reducing agents. In no case, however, was a quantitative yield of benzoic acid obtained, this being due to the fact that benzoic acid itself is slowly destroyed by alkaline reducing agents. No higher yield of benzoic acid was obtained by carrying out the process in an

* This paper corresponds with the abstracts "The action of reducing agents on tannic and gallic acids" and "The action of iodine on phenols and a modified process for the estimation of tannic acid" (*Proc.*, 1908, **24**, 272, 273).

atmosphere of hydrogen or carbon dioxide, and in all cases the complete reduction of tannic and gallic acids occupied a considerable time.

I.—*Reducing Action of Zinc.*

Zinc and Ammonia (Guignet's process).—To 2.5 grams of zinc dust in hot aqueous ammonia was added, with constant shaking, 1 gram of tannic acid dissolved in warm water. After boiling under a reflux condenser for three hours, tannic and gallic acids were absent. Potassium carbonate was then added, the solution boiled to convert the excess of zinc and ammonia into carbonates, then evaporated to dryness and extracted with absolute alcohol. On evaporation, 0.2 gram of pure potassium benzoate was obtained.

With zinc and ammonium chloride, 1 gram of tannic acid gave 0.13 gram of potassium benzoate, whilst zinc with acetic, sulphuric, or hydrochloric acid gave incomplete reduction even after many hours' heating.

With zinc-copper couple, thirteen hours were required for complete conversion, the amount of potassium benzoate obtained from 0.5 gram of tannic acid being 0.14 gram.

Action of Zinc and Ammonia on Benzoic Acid.—One gram of benzoic acid was heated under a reflux condenser for one hour with 2.5 grams of zinc in aqueous ammonia solution. The yield of potassium benzoate was 0.69 gram, an amount which diminished on further heating, thus demonstrating the slow destruction of benzoic acid under the conditions employed.

II.—*Reducing Action of Sodium.*

Sodium and Absolute Alcohol (Böttinger's process).—Two grams of sodium and 1 gram of tannic acid were separately dissolved in absolute alcohol. After heating the mixed solutions for two and a-half hours, no benzoic acid was found, but 0.23 gram of gallic acid was obtained.

Sodium and Moist Ether.—In this case no reduction took place, but gallic acid was formed by hydrolysis.

III.—*Reducing Action of Magnesium.*

Magnesium and Hydrochloric Acid.—One gram of tannic acid gave 0.25 gram of gallic acid, but no benzoic acid.

Magnesium and Ammonium Chloride.—In this case the reaction was very violent, and amounts of potassium benzoate, varying from 0.08 to 0.23 gram, were obtained from 0.5 gram of tannic acid.

Magnesium and Potassium Carbonate.—Here the reaction was moderate, and after heating for five hours on the water-bath the

yield of potassium benzoate was 0.2 gram from 0.5 gram of tannic acid.

Magnesium Powder.—In the above experiment, when magnesium powder was added to the hot solution of tannic acid, a slight action was observed, and therefore the effect of magnesium powder alone was tried. On heating for several hours on the water-bath in a neutral atmosphere, 0.5 gram of tannic acid gave 0.08 gram of potassium benzoate.

IV.—By reaction with aluminium powder and potassium hydroxide, sodium hyposulphite, or hydriodic acid, no formation of benzoic acid occurred.

It is thus seen that in a number of the above experiments the production of benzoic acid was demonstrated, but in no case were the results of quantitative importance, and, although the conditions of concentration, time of reaction, and nature of atmosphere, were widely varied, the results were always unsatisfactory. One general observation was, however, of interest, namely, the tendency of tannic and gallic acids to form reduction products under alkaline conditions, and this is further borne out by experiments made with alkali iodides, which have given much more satisfactory results.

The Action of Iodine on Phenols.

Messinger and Vortmann have shown (*Ber.*, 1890, **23**, 2753) that phenol absorbs iodine in the presence of alkali hydroxides, but were unable to obtain satisfactory quantitative results.

F. Musset (*Chem. News*, 1885, **51**, 42) has described a method of titrating tannin with iodine, but the absorption required twelve hours. The "non-tannins" were estimated in a second experiment after precipitating the tannic acid by means of gelatin.

A. Moullade (*J. Pharm. Chim.*, 1905, [vi], **22**, 153), who titrated tannic acid with iodine in presence of sodium hydrogen carbonate, using carbon disulphide as indicator, states that it is necessary to take the mean of several titrations in order to ensure accuracy, and estimates the non-tannins in the usual manner. All the above-mentioned methods are thus defective, Musset's process requiring at least twelve hours, and that of Moullade being deficient in accuracy.

The modified method which the authors propose, apart from the gelatin precipitation, can be carried out in a few minutes, and concordant results are obtained, not only with tannic acid, but with many other phenolic substances. Within the range of phenols dealt with, a number were found to require one molecule

of iodine for each hydroxyl group, whereas in other cases, although the results were strictly quantitative, they were empirical in the sense that no ratio could be traced between the iodine absorbed and the number of hydroxyl groups.

The general method is as follows. A standard aqueous solution of the phenol is prepared (in the case of tannic acid 1 gram per litre), and to a known volume of this solution (20 c.c., diluted to 200 c.c. with water) *N*/10-iodine solution is added in excess (20 c.c.). A few drops of starch solution are then added, and afterwards aqueous sodium hydroxide is run in drop by drop until the colour due to the iodine disappears. By this means, excess of alkali, which has an injurious effect on the accuracy of the process, is avoided. Dilute hydrochloric or sulphuric acid (1 in 4) is added in sufficient excess (say 50 c.c.) to separate the unabsorbed iodine, the amount of which is estimated by *N*/10-thiosulphate.

In the case of phenol, catechol, quinol, pyrogallol, and gallic acid, the amount of iodine absorbed is exactly one molecule for each hydroxyl group present.

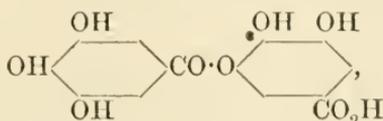
The presence of such groups as NO_2 , NH_2 , or OMe , as well as the position of the hydroxyl groups in the benzene nucleus, was found to have a determining effect on the course of the reaction. For example, the weak phenolic properties of the hydroxyl groups in *p*-hydroxybenzoic acid result in there being no absorption of iodine. The presence of nitro- or methoxy-groups also protects the hydroxyl group from attack, while in *p*-aminophenol a definite quantitative absorption was observed, which, however, did not correspond with one hydroxyl group. The alcoholic hydroxyl group, for example, in benzyl alcohol, is also unaffected under the conditions of the process.

Phloroglucinol, which possesses both phenolic and quinonoid properties, gave an absorption equivalent to two hydroxyl groups, whereas the isomeric pyrogallol behaved normally, the three hydroxyl groups absorbing three molecules of iodine. A similar normal result is obtained with gallic acid.

In the case of gallotannic acid, a large number of experiments were made under varying conditions of concentration, amount of excess of iodine, etc., and perfectly concordant results were always obtained. The process is, therefore, available for the quantitative estimation of gallotannic acid, and is applicable to the commercial tannins. Two estimations are, of course, necessary. First, that of the total iodine absorbed by the standard solution of the tannin, and, secondly, that of the iodine absorbed after removing the tannic acid from the solution by precipitation with gelatin or

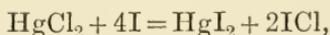
absorption by hide powder, the difference in the two estimations giving the iodine absorbed by the tannic acid itself.

In the case of pure tannic acid, the absorption was found to correspond with 11 atoms of iodine for each molecule of tannic acid. On the supposition that tannic acid may be regarded as digallic acid,



it may be assumed that the chain connecting the benzene nuclei is responsible for the absorption of the additional atom of iodine, the molecule undergoing fission at the chain and forming two molecules of sodium gallate, in one of which an OH group is replaced by OI.

The works of Wys (*Zeitsch. angew. Chem.*, 1898, **11**, 291), Koene (*Pogg. Ann.*, 1845, **66**, 302), and others on the action of Hübl's solution is interesting in connexion with the above recorded observations. Wys attributes the absorption of iodine by unsaturated fatty acids to the presence of iodine monochloride:



which reacts with water, yielding hypoiodous and hydrochloric acids. The hypoiodous acid is slowly transformed into iodic acid and free iodine, the latter again forming iodine monochloride by reacting with the liberated hydrochloric acid. A complicated equilibrium is thus established, the really active substances being contained in the cycle, iodine-iodine chloride-hypoiodous acid.

Koene (*loc. cit.*) has shown that correct iodine values are rapidly obtained by means of the solution produced by shaking alcoholic iodine with finely divided mercuric oxide, which solution contains only mercuric iodide and hypoiodous acid, and Wys has further shown that in the presence of any substance favourable to the formation of hypoiodous acid, for example, iodine, mercuric chloride, or water, iodine absorption takes place more rapidly, whereas the presence of hydrochloric acid or mercuric iodide, which retard the production of hypoiodous acid, have an opposite effect.

The very rapid absorption of iodine in presence of alkali, which occurs in the method for the estimation of phenols suggested in this paper, is very probably due to the formation of hypoiodates.

The action of Hübl's solution on tannic acid has been studied with the view of throwing further light on the question, and a direct connexion between the iodine absorbed from Hübl's solution and that taken up from an alkaline solution has been established. Attempts were also made to isolate iodotannin compounds, but without success. Similar lack of success in this direction has been

recorded by F. B. Power and F. Shedden (*Pharm. J.*, 1901, [iv], 13, 147). These authors consider that true compounds of tannic or gallic acid with iodine cannot be formed by the simple interaction of these compounds in the presence of water, the resulting products containing the iodine in the form of hydriodic acid associated with more or less unaltered tannic or gallic acid and their oxidation products.

Comparison between the results obtained with the iodine process and the Löwenthal method, when applied to a number of the commercial tannin-containing materials, showed a close agreement in all cases.

Experimental Results.

Phenol.—0.1 Gram of phenol was dissolved in 100 c.c. of water. To 10 c.c. of this solution, 5 c.c. of *N*/10-iodine were added, and then a few drops of starch solution. Sodium hydroxide solution was then cautiously added, drop by drop, until the solution became colourless. After stirring, concentrated hydrochloric acid was added, and the separated iodine estimated by standard thiosulphate. The mean of six titrations gave 2.15 c.c. of iodine solution absorbed (=0.0273 gram of iodine). On the supposition that one hydroxyl group requires one molecule of iodine, 0.0272 gram of iodine is theoretically required.

Salicylic Acid.—0.01 Gram of salicylic acid in aqueous solution absorbed 1.85 c.c. (0.0234 gram) of iodine. Calculated for one hydroxyl group, the theoretical absorption is 0.0184 gram of iodine. The result in this case is, therefore, empirical, although repeated estimations proved it to be quantitative.

Messinger and Vortmann (*loc. cit.*), following Kopperschaar's process for the estimation of phenol by bromine, proposed to estimate salicylic acid by precipitating it in alkaline solution, as sodium di-iodoiodososalicylate, by addition of iodine and titrating the excess of iodine with sodium thiosulphate. W. Fresenius and Grünhut (*Zeitsch. anal. Chem.*, 1899, 38, 292) have criticised this method adversely, but in our experiments the results were remarkably consistent, and the results were unaffected by the concentration of the solution or the amount of excess of iodine or of sodium hydroxide. Moreover, the method is available for the estimation of salicylic acid in the presence of benzoic acid.

Resorcinol.—0.01 Gram of resorcinol absorbed 5.2 c.c. (0.06604 gram) of iodine. The theoretical amount of iodine representing three molecules is 0.0694 gram.

Catechol.—0.01 Gram required 3.65 c.c. of *N*/10-iodine (0.0461 gram). Theory for two hydroxyl groups=0.0463 gram. In this case, therefore, the reaction may be considered normal.

Quinol.—0.01 Gram required 3.6 c.c. of *N*/10-iodine (0.0456 gram). Theory requires 0.0463 gram. Of the three isomeric dihydroxybenzenes, therefore, the ortho- and para-compounds behave normally, whereas the meta-derivative gives somewhat empirical results.

Pyrogallol.—0.01 Gram required 6.1 c.c. of *N*/10-iodine, which corresponds almost exactly with three hydroxyl groups on the supposition that one molecule of iodine is required for each hydroxyl group.

Gallic Acid.—0.01 Gram required 3.55 c.c. of *N*/10-iodine (0.0448 gram). Theory for three hydroxyl groups=0.0450 gram.

Catechu-tannic Acid.—0.01 Gram in four titrations absorbed 3 c.c., 2.9 c.c., 3.1 c.c., and 2.9 c.c. respectively of *N*/10-iodine. The method is, therefore, available in this case.

Catechin.—0.01 Gram required 2.4 c.c. of *N*/10-iodine (0.033 gram). Calculation for five hydroxyl groups gives 0.035 gram of iodine.

Influence of the Presence of other Groups on the Iodine Absorption.

Ortho- and para-nitrophenols do not absorb iodine under the conditions, showing the protective action of the nitro-group. Picric acid is also inactive. In the case of *p*-aminophenol, 0.01 gram absorbed only 0.35 c.c. of *N*/10-iodine (0.00444 gram). This corresponds with approximately one molecule of iodine for each four molecules of *p*-aminophenol. The result clearly shows the influence of the amino-group, and the method in this and similar cases is useless. Some absorption of iodine also takes place in the case of aminonaphthol-4-sulphonic acid. The non-absorption of iodine by mannitol, benzyl alcohol, and other compounds containing alcoholic groups, shows that the method is not available in the case of aliphatic hydroxyl groups. In the case of phloroglucinol, which can behave either as a phenol or as a quinone, 0.01 gram absorbed 0.04318 gram of iodine, which closely corresponds with two instead of the three hydroxyl groups actually present. The protective action of the methoxy-group is indicated in the case of vanillin, with which no absorption takes place. The influence of the position of the hydroxyl group is well shown in the case of the hydroxybenzoic acids. No reaction takes place with the *p*-derivative, but with salicylic acid, as already noted, quantitative results were obtained. This difference is probably associated with the pronounced phenolic character of salicylic acid exhibited in its antiseptic properties, its low melting point, its reaction with ferric chloride, its ready solubility in chloroform, and its slight solubility

in water, in which properties it is in marked contrast to its isomerides.

Cinnamic Acid.—This unsaturated acid, which contains no hydroxyl group, does not absorb iodine from alkaline solution.

Tannic Acid.—For the experiments with this substance, a sample of pure tannic acid (Kahlbaum) was used. 0.02 Gram required, as the mean of a large number of closely agreeing titrations, 7.15 c.c. of *N*/10-iodine. After precipitating the tannic acid by gelatin, an absorption of 0.3 c.c. of *N*/10-iodine was given by 20 c.c. of the residual solution. The corrected amount of iodine absorbed was therefore = 0.08698 gram. 0.02 Gram of tannic acid requires for five hydroxyl groups 0.0788 gram of iodine ($5I_2$), and for six hydroxyl groups 0.0946 gram ($6I_2$). On the supposition that 11 atoms are absorbed by one molecule of gallotannic acid, the amount of iodine required by 0.02 gram of gallotannic acid is 0.0876 gram, which figure is in practical agreement with the experiments. The purity of the tannic acid was, however, not known.

In order to test the reliability of the method, a large number of results were obtained, using widely differing quantities of the substances. The method was also applied to a number of the ordinary tannin-containing materials, the results obtained being compared with those given by the Löwenthal process. The solution of tannic acid contained 1 gram per litre:

Volume of tannic acid solution, c.c....	40	35	30	25	20	15	10	5
,, <i>N</i> /10-iodine, c.c.	14.25	12.45	10.70	8.90	7.15	5.35	3.55	1.80

In each case the solution was diluted to 200 c.c. with water.

The experiments were repeated, using *N*/50-iodine and *N*/50-sodium thiosulphate:

Volume of tannic acid solution, c.c.	20	15	10	5
,, <i>N</i> /50-iodine expressed as sodium thio- sulphate, c.c.	34.87	26.30	17.53	8.76

Comparison of the Iodine with the Löwenthal Method.—The results (p. 1827) are expressed in percentages of tannic acid, Kahlbaum's pure tannic acid being taken as the standard.

Comparison of the Iodine Method with Hübl's Process.—0.2 Gram of tannic acid was dissolved in 25 c.c. of alcohol, and 25 c.c. of chloroform, followed by 25 c.c. of Hübl solution, were added. After standing twenty-four hours, the *N*/10-iodine absorbed was 33.55 c.c., the figures in sixteen experiments varying from 32.35 c.c. to 35.25 c.c. A similar series, in which the chloroform was omitted, gave 32.46 c.c. of *N*/10-iodine absorbed. The amount taken up by 0.2 gram of tannic acid under alkaline conditions is 71.5 c.c. of *N*/10-iodine, which is almost double the above figure.

Tannins.		Löwenthal method.	Iodine method.
Gall-nuts	No. 1 Extract.....	66·47	65·3
	No. 2 ,,	64·02	65·62
	No. 3 ,,	60·40	60·28
	No. 4 ,,	63·61	63·14
	No. 5 ,,	62·59	62·09
Sumac	No. 1 Extract.....	22·84	21·26
	No. 2 ,,	22·51	20·14
	No. 3 ,,	16·57	16·08
	No. 4 ,,	17·20	16·78
Myrabolams...	No. 1 Extract.....	26·06	27·27
	No. 2 ,,	27·52	27·44
	No. 3 ,,	29·33	29·74
	No. 4 ,,	31·24	31·12
Valonia.....		28·11	28·67
Dividivi		33·00	31·47
Quebracho		13·63	13·28

General Conclusions.

The absorption of iodine by phenols in alkaline solution appears, in certain cases, to take place in definite molecular proportions, but in other cases in empirical, although quantitative, amount. The absorption takes place most readily in the case of compounds with pronounced phenolic properties, and is, in some cases, entirely prevented by the presence of other groups in the benzene nucleus. The method described is, however, available for the quantitative determination of tannic acid and other substances, and involves no complicated or lengthy process or the observation of an indefinite end-point. It appears, therefore, to be of practical importance.

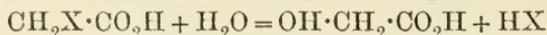
TECHNICAL RESEARCH LABORATORY,
TECHNICAL COLLEGE,
BRADFORD.

CCIII.—*Reactivity of the Halogens in Organic Compounds. Part III. Interaction of Bromoacetic, α -Bromopropionic, and α -Bromobutyric Acids and their Sodium Salts with Water and with Alkali.*

By GEORGE SENTER.

IN previous papers (Trans., 1907, 91, 460; Proc., 1908, 24, 89; *Arrhenius Festschrift*, 1909, Vol. II) the results of an experimental investigation of the rate of displacement of the halogens in chloroacetates and bromoacetates have been given, and the mechanism of

the respective reactions was discussed. Reasons have been adduced for the opinion that in the hydrolytic decomposition of chloro- and bromo-acetic acids by water, according to the equation :



(X = Cl or Br), the reaction takes place mainly between the non-ionised acid and non-ionised water. This view as to the mechanism of these reactions is further discussed in the present paper in connexion with the corresponding measurements with the higher and substituted fatty acids.

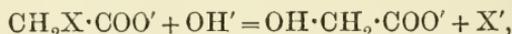
The decomposition of the sodium salts of the halogenacetic acids by water and by alkali, represented by the general equations



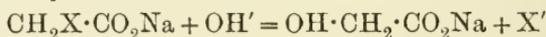
and



appears to be rather complicated. The experimental results are most readily accounted for on the view that in case (1) the main reaction in dilute solution takes place between $\text{CH}_2\text{X}\cdot\text{COO}'$ ions and non-ionised water, but in more concentrated solutions the reaction of the sodium salt, $\text{CH}_2\text{X}\cdot\text{CO}_2\text{Na}$, with water becomes of importance. For reactions of type (2) the mechanism in dilute solution is represented by the equation :



but in moderately concentrated solutions the reaction



also comes into account.

The present paper deals with the displacement of the bromine in the first three members of the series of α -bromo-fatty acids and their sodium salts, the results obtained with bromoacetic acid having been partly repeated for the sake of comparison. As the mechanism of the reactions has already been discussed in connexion with the lowest members of the series, it has not been considered necessary, in the case of the higher acids, to vary the experimental conditions so widely, and attention has mainly been directed to the influence of substitution on the reactivity of the halogen. The results show that even in compounds so similar in type as the α -bromo-fatty acids, there are remarkable differences in the relative reactivity of the halogen according to the method by which it is measured.

EXPERIMENTAL.

Hydrolytic Decomposition of the Bromo-fatty Acids by Water.—The results of a typical series of experiments with bromoacetic acid, α -bromopropionic acid, and α -bromobutyric acid at 81° are given in

table I. The acids were employed in approximately $N/10$ -solution; quantities of 10 c.c. were sealed up in small tubes of Jena glass, and placed in a thermostat at constant temperature. At intervals tubes were taken out, rapidly cooled, and the contents titrated with a dilute solution of barium hydroxide, using phenolphthalein as indicator. In the tables the concentrations, C_t , are given in c.c. of the barium hydroxide solution required to neutralise the bromo-acid remaining in 10 c.c. of the solution after heating for the time t . The "constants," k , are calculated according to the formula for a unimolecular reaction, $0.4343k = 1/t \log_{10} C_0/C_t$, where C_0 is the initial concentration.

TABLE I.—Temperature 81°.

Bromoacetic acid, $N/10$.			α -Bromopropionic acid, $N/10$.		α -Bromobutyric acid.	
t (min.).	C_t .	k .	C_t .	k .	C_t .	k .
0	11.4	—	12.6	—	11.8	—
60	10.3	0.0017	10.2	0.0035	8.9	0.0043
150	9.1	0.0015	8.5	0.0026	7.3	0.0032
270	7.7	0.0014	6.8	0.0023	6.0	0.0025

These results illustrate two important points: (1) the initial rate at which the bromine is displaced increases somewhat with the complexity of the acid; (2) whilst the "constants" for bromoacetic acid diminish slowly, those for the remaining acids diminish rapidly as the reaction proceeds. As it seemed probable that this diminution in the value of the constants might be connected with the presence of the hydrobromic acid formed in the course of the reaction, several series of experiments were made in the presence of different concentrations of hydrobromic acid, added at the commencement of the reaction. The results are given in the accompanying table.

TABLE II.

 α -Bromopropionic Acid, $N/10$.—Temperature 79°.

No hydrobromic acid.			0.10 <i>N</i> -Hydrobromic acid.		0.20 <i>N</i> -Hydrobromic acid.	
t .	C_t .	k .	C_t .	k .	C_t .	k .
0	11.8	—	11.8	—	11.8	—
120	8.8	0.0024	10.4	0.00105	10.8	0.00074
240	7.3	0.0020	9.4	0.00095	9.9	0.00074
360	6.3	0.0017	8.8	0.00082	9.1	0.00073
1380	2.2	0.0012	3.9	0.00080	4.6	0.00069

0.40 <i>N</i> -Hydrobromic acid.			0.80 <i>N</i> -Hydrobromic acid.		
t .	C_t .	k .	t .	C_t .	k .
0	11.8	—	0	11.8	—
180	10.5	0.00065	240	10.4	0.00053
360	9.4	0.00064	1335	5.8	0.00053
1380	5.3	0.00061			

In another series of measurements at the same temperature, in the presence of 0.27*N*-hydrobromic acid, the value of *k* was 0.0068, in good agreement with the above results.

The data just given show that in the absence of hydrobromic acid the reaction is comparatively rapid, but as the acid accumulates in the system, the rate rapidly diminishes. Further, in the presence of 0.20*N*-hydrobromic acid, constants agreeing well for a unimolecular reaction are obtained, and addition of more acid has comparatively little effect on the reaction velocity. The bearing of these results on the mechanism of the reaction is discussed in detail later (p. 1836).

As regards the effect of hydrobromic acid on the rate of decomposition of bromobutyric acid by water, it will be sufficient to quote the result of one series of experiments.

TABLE III.

α-Bromobutyric Acid, *N*/10.—Temperature 79°.

No hydrobromic acid.			0.27 <i>N</i> -Hydrobromic acid.		
<i>t.</i>	<i>C_t</i>	<i>k.</i>	<i>t.</i>	<i>C_t</i>	<i>k.</i>
0	11.6	—	0	11.6	—
60	9.5	0.0033	150	10.9	(0.00042)
150	8.3	0.0022	360	10.3	0.00033
360	6.3	0.0017	1380	7.2	0.00035
1380	3.0	0.0010			

These results show that the rate of decomposition of bromobutyric acid by water diminishes still more rapidly than that of bromopropionic acid, and, in agreement with this, that hydrobromic acid in equivalent concentrations retards the former reaction still more than the latter.

N/4-Hydrobromic acid reduces the constant for bromoacetic acid from 0.0062 to 0.0057 at 102°.

Influence of Neutral Salts.—The effect of neutral salts on the rate of hydrolysis of the bromo-fatty acids by water is very slight, as the following results show. The constants are calculated from a rather advanced stage of the reactions, when the value for bromobutyric acid is less than that for bromopropionic acid.

TABLE IV.—Temperature 79°.

<i>α</i> -Bromopropionic acid, <i>N</i> /10.		<i>α</i> -Bromobutyric acid, <i>N</i> /10.	
Salt added.	<i>k.</i>	Salt added.	<i>k.</i>
No salt	0.0013	No salt	0.0010
+ <i>M</i> /1-Sodium bromide..	0.0012	+ <i>M</i> /1-Sodium bromide..	0.0009
+ <i>M</i> /1-Sodium nitrate ...	0.0012	+ <i>M</i> /1-Sodium nitrate ...	0.0010

Reaction between Sodium Salts and Water.

The sodium salts were prepared in dilute solution by careful neutralisation of the acids with sodium hydroxide, free from carbonate. The solutions, which were approximately $N/10$, were heated for definite intervals in sealed tubes at constant temperature, and the contents of the tubes titrated with barium hydroxide and phenolphthalein. The concentrations, C_t , are expressed as the number of c.c. of the standard barium hydroxide solution which would be required to neutralise the acid equivalent to the amount of salt in 10 c.c. of the solution after the time t has elapsed. The values of k are calculated according to the integrated equation,

$$0.4343k = 1/t \log_{10} C_0/C_t,$$

for a unimolecular reaction.

TABLE V.—Temperature 52.4°.

Sodium bromoacetate, $N/10$.			Sodium α -bromopropionate, approx. $N/10$.		
t (min.).	C_t .	k .	t (min.).	C_t .	k .
0	11.0	—	0	12.4	—
1560	9.4	0.00010	60	11.4	0.0014
3120	7.9	0.00010	120	10.7	0.0012
4440	6.9	0.00010	240	9.5	0.0011

Sodium α -bromobutyrate, $N/10$.		
t .	C_t .	k .
0	10.9	—
60	9.3	0.0026
120	8.5	0.0023
240	7.3	0.0017

The table shows that sodium bromoacetate and sodium bromopropionate give fairly good constants for a reaction of the first order, although in the latter case there is a slight diminution as the reaction proceeds. In the case of sodium bromobutyrate the diminution in the magnitude of the constants is still greater. As it seemed probable that this might be due to the influence of the sodium bromide formed in the course of the reaction, some measurements were made in the presence of this salt, and the results are given in table VII.

As the results obtained with sodium chloroacetate described in the previous paper appear to show that both the ions $\text{CH}_2\text{Cl}\cdot\text{COO}'$ and the non-ionised salt, $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Na}$, react with water, it was considered desirable to make some comparative measurements with sodium bromopropionate and butyrate in $N/10$ - and $N/100$ -solution; in the latter dilution the salts are almost completely ionised. The results are summarised in table VI, and show that the reactions are rather more rapid in the more dilute solutions.

TABLE VI.—Temperature 52·4°.

Sodium bromoacetate.		Sodium bromopropionate.		Sodium bromobutyrate.	
Dilution.	<i>k</i> .	Dilution.	<i>k</i> .	Dilution.	<i>k</i> .
N/10	0·00010	N/10	0·0012	N/10	0·0023
N/100	0·00010	N/100	0·0014	N/100	0·0026

The bearing of these important results on the mechanism of the reaction is discussed later (p. 1837).

Influence of Neutral Salts.—As in the case of the free acids, the effect of sodium bromide and of sodium nitrate on the reactions has been investigated, with the following results :

TABLE VII.—Temperature 52·4°.

Sodium α-Bromopropionate, N/10.

<i>t</i> (min.).	No salt added.		M/1-Sodium bromide.		M/1-Sodium nitrate.	
	<i>C_t</i> .	<i>k</i> .	<i>C_t</i> .	<i>k</i> .	<i>C_t</i> .	<i>k</i> .
0	13·4	—	13·4	—	13·4	—
90	11·7	0·0015	12·2	0·0010	11·9	0·0014
330	8·6	0·0014	10·0	0·0009	8·9	0·0013

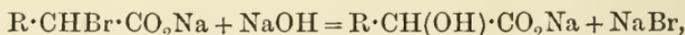
Sodium α-Bromobutyrate, N/10.

<i>t</i> (min.).	No salt added.		M/1-Sodium bromide.		M/1-Sodium nitrate.	
	<i>C_t</i> .	<i>k</i> .	<i>C_t</i> .	<i>k</i> .	<i>C_t</i> .	<i>k</i> .
C	11·7	—	11·7	—	11·7	—
90	9·4	0·0024	9·9	0·0019	9·6	0·0022
330	6·3	0·0020	7·8	0·0013	6·7	0·0017

These results indicate that, whilst the rate of the reactions is only slightly diminished by the addition of sodium nitrate, both reactions are considerably retarded by sodium bromide (compare p. 1838).

Reaction between Sodium Salts and Alkali.

The chemical changes in this case are expressed by the general equation :



where R represents hydrogen or an alkyl group. Dilute solutions of the sodium salts were mixed with an equivalent amount of alkali, and, after heating in sealed tubes for definite intervals, were titrated with approximately N/10-sulphuric acid and phenolphthalein. In all cases the sodium salt and the alkali were present in equivalent proportions, and the concentrations are expressed as the number of c.c. of acid

required to neutralise 10 c.c. of the reaction mixture. The values of k for the bromoacetate are calculated according to the general equation for a bimolecular reaction,

$$k = \frac{1}{tC_0} \cdot \frac{C_t}{C_0 - C_t}$$

when the reacting substances are present in equivalent amounts.

TABLE VIII.—Temperature 52.4°.

Sodium bromoacetate and hydroxide, $N/10$.			Sodium bromopropionate and hydroxide, $N/10$.		Sodium bromobutyrate and hydroxide, $N/10$.	
t .	C_t .	k .	C_t .	k .	C_t .	k .
0	11.8	—	13.6	—	11.6	—
60	8.5	0.00055	11.8	—	9.6	—
180	5.5	0.00054	9.6	—	7.4	—
300	4.3	0.00050	7.9	—	6.2	—

The figures show that in the presence of sodium hydroxide, bromine is displaced from sodium bromoacetate more rapidly than from the other two salts, and that for the former reaction constants agreeing well for a bimolecular change are obtained. On comparing the numbers found for sodium bromopropionate and bromobutyrate with those obtained for the same salts with water alone, it will be seen that the speed in the latter case is not much less than when alkali is present. Hence it is not justifiable to calculate the results on the assumption that only the reaction between the salts and alkali is of importance (as in the case of sodium bromoacetate); we are dealing with two simultaneous reactions, in which the salts are acted on by water and by alkali. The calculation of the experimental results on this basis is dealt with in a later part of the paper.

Influence of Neutral Salts.—In the former paper it was shown that the rate of reaction between sodium bromoacetate and sodium hydroxide is greatly accelerated by the action of neutral salts. In the same way the effect of neutral salts on the reaction between sodium hydroxide and sodium bromopropionate and bromobutyrate respectively has been investigated; the results are given in table IX.

TABLE IX.—Temperature 52.4°.

<i>Sodium Bromopropionate and Hydroxide, N/10.</i>			
No neutral salt.		$M/1$ -Sodium bromide.	$M/1$ -Sodium nitrate.
t .	C_t .	C_t .	C_t .
0	13.4	13.4	13.4
90	11.2	11.2	11.1
240	8.3	8.9	7.8

TABLE IX.—Temperature 52.4° (*continued*).*Sodium α -Bromobutyrate and Hydroxide, N/10.*

No neutral salt.		M/1-Sodium bromide.	M/1-Sodium nitrate.
0	11.7	11.7	11.7
90	10.0	10.3	9.8
240	7.8	8.6	7.5

These results are rather difficult to interpret, as we are dealing with two simultaneous reactions which are presumably differently influenced by neutral salts.

DISCUSSION OF RESULTS.

Reactivity of Bromine in the Different Compounds.—It will be of interest before dealing with the individual reactions to represent in tabular form the relative velocity with which bromine is displaced from the three acids and their salts under equivalent conditions. The measurements have not all been made at the same temperature, but by means of the temperature-coefficients given in the previous paper (*Arrhenius Festschrift, loc. cit.*), and on the provisional assumption that the coefficients for reactions of the same type are equal, the results are calculated to a uniform temperature of 52.4°. As regards the magnitude of the velocity constants, the reactions between the acids and water, and the sodium salts and water respectively, are unimolecular, and the constants are therefore independent of the units in which the concentrations are expressed. This, however, is not the case for the bimolecular reaction between the salts and sodium hydroxide. The unit employed was that equivalent to 1 c.c. of 0.085*N*- (or 1/11.8*N*) sulphuric acid, 10 c.c. of the reaction mixture being titrated, and therefore to a concentration of $1/11.8 \times 10 = 1/118$ gram-molecule per litre. Hence, if referred to 1 gram-mol. per litre, the constants in table VIII have to be multiplied by 118, if (as is more suitable for our present purpose) the unit is 1/10 gram-molecule per litre, they have to be multiplied by 11.8. For the sake of completeness, constants representing the rate of the reaction between the bromo-acids and silver nitrate are included; the results of this investigation will be given in a subsequent communication.

TABLE X.—Temperature 52·4°.

$\text{CH}_2\text{Br}\cdot\text{CO}_2\text{H} + \text{H}_2\text{O}.$ $k = 0\cdot000085$ [1]	$\text{CHMeBr}\cdot\text{CO}_2\text{H} + \text{H}_2\text{O}.$ $0\cdot00017$ [2]	$\text{CHEtBr}\cdot\text{CO}_2\text{H} + \text{H}_2\text{O}.$ $0\cdot00022$ [2·6]
$\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Na} + \text{H}_2\text{O}.$ $k = 0\cdot00010$ [1·2]	$\text{CHMeBr}\cdot\text{CO}_2\text{Na} + \text{H}_2\text{O}.$ $0\cdot0014$ [16]	$\text{CHEtBr}\cdot\text{CO}_2\text{Na} + \text{H}_2\text{O}.$ $0\cdot0026$ [30]
$\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Na} + \text{NaOH}.$ $k = 0\cdot0065$ [76]	$\text{CHMeBr}\cdot\text{CO}_2\text{Na} + \text{NaOH}.$ $0\cdot0009$ [10]	$\text{CHEtBr}\cdot\text{CO}_2\text{Na} + \text{NaOH}.$ $0\cdot0008$ [9]
$\text{CH}_2\text{Br}\cdot\text{CO}_2\text{H} + \text{AgNO}_3.$ $k = 0\cdot0064$ [76]	$\text{CHMeBr}\cdot\text{CO}_2\text{H} + \text{AgNO}_3.$ $0\cdot48$ [5700]	$\text{CHEtBr}\cdot\text{CO}_2\text{H} + \text{AgNO}_3.$ $1\cdot44$ [17000]

The numbers in brackets give the relative initial velocities of the reactions in $N/10$ -solution referred to the slowest—the reaction between bromoacetic acid and water—as unit.

Interaction of the α -Bromo-fatty Acids and Water.

This type of reaction, which may be represented by the general equation $\text{R}\cdot\text{CHX}\cdot\text{CO}_2\text{H} + \text{H}_2\text{O} = \text{R}\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H} + \text{HX}$, has been fully investigated in the case of chloroacetic acid and water (Trans., 1907, 91, 460). As the addition of free halogen acid has very little effect on the rate of reaction, I have already suggested that the main change takes place between the non-ionised acid and water, the reaction, unlike most hydrolytic changes, not being catalytically accelerated by H^+ ions. Bodenstein (*Zeitsch. Elektrochem.*, 1909, 15, 403) has recently suggested an alternative explanation of these observations—to the effect that it is the $\text{CH}_2\text{Cl}\cdot\text{COO}'$ ion which is acted on by water, and that the effect of the hydrochloric acid in diminishing the ionisation of the chloroacetic acid (and thus diminishing the $\text{CH}_2\text{Cl}\cdot\text{COO}'$ ion concentration) is just balanced by its catalytic effect. In support of this suggestion it is stated that with one exception, the hydrolytic decomposition of certain sulphonic esters (Wegscheider, *Zeitsch. physikal. Chem.*, 1902, 41, 52), all hydrolytic actions are accelerated by acids.

There appear, however, to be certain objections to Bodenstein's view as to the mechanism of these reactions. The effect of acids in accelerating hydrolytic changes is by no means general. I have recently shown (*Proc., loc. cit.*; *Arrhenius Festschrift, loc. cit.*) that the hydrolytic decomposition of α -chlorohydrin by water is only slightly affected by hydrochloric acid, and as in this case there is no ionisation, we have a reaction, closely analogous to that under discussion, in which H^+ ions exert no catalytic effect. Further, the remarkable results

obtained in the investigation of the hydrolytic decomposition of α -bromopropionic acid and α -bromobutyric acid by water, described in the present paper, appear very difficult to account for on Bodenstein's theory, but are readily explained on the view as to the mechanism of these reactions I have advocated. It has been shown that when the acids alone are heated with water, the "constants" calculated for a unimolecular reaction diminish fairly rapidly, but in the presence of excess of hydrobromic acid constants agreeing well for a unimolecular reaction are obtained. The most rational explanation of this observation is that both the free $\text{CHMeBr}\cdot\text{COO}'$ ions and the non-ionised acid are acted on by water. If we call the constant for the first reaction k_1 , and that for the second reaction k_2 , the rate of the reaction is represented by the differential equation :

$$\frac{d[\text{HBr}]}{dt} = k_1[\text{CHMeBr}\cdot\text{COO}'][\text{H}_2\text{O}] + k_2[\text{CHMeBr}\cdot\text{CO}_2\text{H}][\text{H}_2\text{O}] \quad (1),$$

(a.) (b.)

where $d[\text{HBr}]/dt$ represents the rate at which hydrobromic acid is liberated, in other words, the rate of the reaction as a whole. When free bromopropionic acid is taken, the factor (a) is of importance (it being assumed that the ion reacts more rapidly with water than the free acid), but as hydrobromic acid accumulates in the system, (a) becomes smaller and smaller, and finally becomes negligible in comparison with (b). This suggestion as to the mechanism of the reaction can be tested by calculating the initial concentration of $\text{CHMeBr}\cdot\text{COO}'$ ions in the free acid solution, and hence the initial velocity of the reaction, which is the sum of the rate of hydrolytic decomposition of the non-ionised acid and of the ions. The latter factor can be determined approximately from the rate of decomposition of sodium bromopropionate, and the former by extrapolation from the rate in the presence of excess of hydrobromic acid. The constant for sodium bromopropionate in $N/10$ -solution at 52.4° is 0.0014, and, assuming that the temperature-coefficient for 10° is 3.0, the approximate value of the constant at 79° will be 0.035. At 79° a $N/10$ -solution of bromopropionic acid is ionised to the extent of about 10 per cent., and the sodium salt to 80 per cent. Hence, the ratio of the $\text{CHMeBr}\cdot\text{COO}'$ ion concentrations in the two solutions is 8:1, and the constant for the free acid, as far as the ions are concerned, is $0.035/8 = 0.0044$. To this has to be added the constant for the non-ionised acid, which, in the absence of hydrobromic acid, will be approximately 0.0007 (Table II). Hence, the initial velocity at 79° should be $0.0044 + 0.0007 = 0.0051$, and should diminish fairly rapidly, owing to the formation of hydrobromic acid and the consequent diminution in the concentration of the $\text{CHMeBr}\cdot\text{COO}'$ ions. In good agreement with this, the observed average value of the constant during the first hour

is about 0.0030. It is not practicable in such a case to determine with accuracy the initial velocity by titration after heating for a short interval of time, as some time elapses before the tubes assume the temperature of the bath, and considerable uncertainty is thus introduced.

The view as to the mechanism of the reactions advocated in the previous paper not only accounts for the fall in the constants for the two higher acids, but also for the fact that fairly well agreeing constants are obtained for bromoacetic acid throughout the reaction. In the latter case, the reactivity of the $\text{CH}_2\text{Br}\cdot\text{COO}'$ ion with water is comparatively so small (compare table V) that the (a) term in equation (1) is negligible throughout.

A very interesting point in connexion with the bromo-fatty acids is that the effect of hydrobromic acid in diminishing the rate at which bromine is displaced becomes greater as the series is ascended. This result is not directly connected with the "strength" of the acids. The dissociation constants at 25° are as follows: Bromoacetic acid 0.00138, α -bromopropionic acid 0.00108, α -bromobutyric acid 0.00106. Thus the two latter acids are equal in strength, whereas the ratio of the rates of displacement of bromine in the presence of $N/5$ -hydrobromic acid is approximately 2 : 1. Whether these represent the intrinsic rates of displacement for the non-ionised acids, or whether the acids are affected directly by hydrobromic acid to a different extent, is not easy to decide. Experiments are in progress with the object of throwing light on this question.

Interaction of the Sodium Salts and Water.

The results given on p. 1831, especially the observation that the velocity constants are rather greater in $N/100$ -solution than in $N/10$ -solution, show conclusively that, at least in dilute solution, the negative ion, and not the non-ionised salt, is the active agent. Hence there appear to be only two possible methods of representing the mechanism of the reactions :

(1) The anion $\text{R}\cdot\text{CHBr}\cdot\text{COO}'$ reacts directly with water according to the equation $\text{R}\cdot\text{CHBr}\cdot\text{COO}' + \text{H}_2\text{O} = \text{R}\cdot\text{CH}(\text{OH})\cdot\text{COO}' + \text{HBr}$.

(2) The bromine is displaced along with the negative electron, as represented by the typical equation :



the residue immediately uniting with water to form the corresponding hydroxy-fatty acid, $\text{R}\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$. The first alternative is rather difficult to reconcile with the fact that the velocity increases with the complexity of the anion, the ratio bromoacetate : bromopropionate : bromobutyrate being approximately 1 : 14 : 26 (table X). The fact

that the methyl group is, in general, more positive than hydrogen can scarcely account for the fact that the $\text{CHMeBr}\cdot\text{COO}'$ ion is fourteen times more reactive than the $\text{CH}_2\text{Br}\cdot\text{COO}'$ ion, more especially as the introduction of larger groups might be expected to retard the action owing to "steric hindrance."

On the alternative view as to the mechanism of the reaction, a plausible explanation of the accelerating effect of substitution can be given. It is well known (compare Van't Hoff, *Vorlesungen*, III, p. 131) that the tendency of maleic acid to eliminate water, forming the anhydride, is greatly increased by substituting methyl groups for hydrogen, for example, dimethylmaleic acid is only known in the form of the anhydride, $\begin{array}{c} \text{CMe}\cdot\text{O} \\ | \\ \text{CMe}\cdot\text{O} \end{array} > \text{O}$, and the usual explanation is that

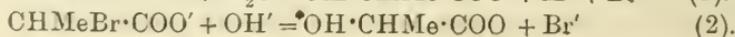
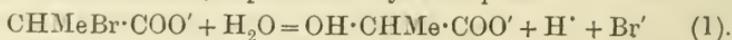
owing to the greater space occupied by the larger substituting groups the two carbonyl groups are urged nearer together, the removal of water between the two groups being thus facilitated. On similar

lines it may be suggested that in the compound $\begin{array}{c} \text{R}\cdot\text{CHBr} \\ | \\ \text{OCO}' \end{array}$ the bromine atom and the negative electron are urged nearer in space the larger the group R, thus facilitating the formation of Br' ions. If this reaction is to any extent reversible, the addition of alkali bromides ought to retard it, and, in accordance with this, it has already been pointed out that reactions of this type are considerably retarded by sodium bromide (p. 1832).

Interaction of the Sodium Salts and Sodium Hydroxide.

The results given in the present and former papers appear to show that, as regards the first member of the series, bromoacetic acid, the reaction between its sodium salt and sodium hydroxide in dilute solution is best represented by the equation $\text{CH}_2\text{Br}\cdot\text{COO}' + \text{OH}' = \text{CH}_2(\text{OH})\cdot\text{COO}' + \text{Br}'$. A remarkable difference between the reaction and that of ester saponification, however, is that in the former case the $\text{CH}_2\text{Br}\cdot\text{COO}'$ ion is acted on almost as rapidly by water as by dilute alkali.

The results quoted in table VIII show that the sodium salts of the two higher bromo-fatty acids are acted on less rapidly in the presence of alkali than is sodium bromoacetate. Comparison with the data in table V shows that for the former two salts the action of water cannot be neglected in comparison with that of alkali. In the case of sodium α -bromopropionate, for example, we are dealing with two simultaneous reactions, represented by the equations:



If dx/dt represents the rate at which bromine is displaced as the result of the simultaneous reactions (1) and (2), the rate of the reaction is represented by the differential equation :

$$\frac{dx}{dt} = k_1[\text{CHMeBr}\cdot\text{COO}'][\text{H}_2\text{O}] + k_2[\text{CHMeBr}\cdot\text{COO}'][\text{OH}'] \quad (3).$$

If the salt and sodium hydroxide are taken in equivalent concentration, and the latter, at the time t , is represented by $a - x$, equation (3) simplifies to

$$\frac{dx}{dt} = k_1(a - x) + k_2(a - x)^2 = [k_1 + k_2(a - x)](a - x) \quad (4),$$

the concentration of the water being taken as constant.

On integrating equation (4), putting $x=0$ when $t=0$, we obtain

$$k_1 t = 2.3026 \log_{10} \frac{[k_1 + k_2(a - x)]a}{(a - x)(k_1 + k_2 a)} \quad (5).$$

These formulæ must now be applied to the experimental results given in table VIII. Perhaps the simplest method of procedure is to find an approximate value for k_2 by substituting in equation (4) known values of $(a - x)$ and k_1 (the latter being obtained at once from the results given in table V), and to check these values by means of equation (5). In this way, $k_2 = 0.00008$ has been obtained as the average value of the velocity constant for the reaction between sodium bromopropionate and sodium hydroxide, and $k_2 = 0.00007$ as the corresponding constant for the reaction between sodium bromobutyrate and sodium hydroxide. In order to reduce these numbers to a concentration of 1/10 molecule per litre, they have to be multiplied by 11.8 (compare p. 1834), and thus the values $k_2 = 0.0009$ and 0.0008 quoted in table X are obtained.

A little difficulty in checking these values by substitution in equation (5) arises from the fact that k_1 diminishes somewhat throughout the reaction owing to the retarding influence of the products of the reaction. It has therefore not been considered necessary to quote the results of the calculations in detail, as the numbers given are sufficiently accurate for our present purpose.

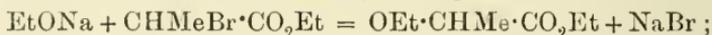
Two interesting results have thus been obtained: (1) that in contrast to ester hydrolysis the action of alkali on the sodium salts of the bromo-fatty acids is not much more rapid than the action of water alone; (2) there is a fall in reaction velocity with increasing substitution, the ratio bromoacetate: α -bromopropionate: α -bromobutyrate being approximately 9:1.1:1. The first observation becomes more intelligible when it is borne in mind that, whereas in ester saponification a negatively charged group (the OH' group) is acting on a neutral molecule, in the case now under discussion the reaction takes place between two negatively charged groups (compare Meyer, *Zeitsch.*

physikal. Chem., 1909, 67, 257). In the latter case, the repelling effect of the two similar charges may well exert a great retarding influence on the reaction velocity. This view becomes still more plausible when it is borne in mind that the action of alkali on the electrically neutral α -chlorohydrin is enormously more rapid than that of water, just as in ester hydrolysis (Senter, *loc. cit.*).

The diminution in the velocity as the series is ascended is perhaps most readily accounted for on space considerations, the action of OH' ions on the bromine being the more retarded the greater the volume of the substituting group.

General Conclusions.

There do not appear to be any previous results with which those given in the present paper can be directly compared. Bischoff (*Ber.*, 1899, 32, 1748) carried out an extensive series of experiments on the reaction between sodium alkyl oxides and bromo-fatty esters. In the case of sodium ethoxide and bromopropionic ester, for example, the main reaction may be represented by the equation



but secondary reactions, such as hydrolysis of the bromo-fatty ester, also occur in this and the corresponding reactions with other esters and alkyl oxides. For two reasons, Bischoff's results cannot be regarded as giving a very satisfactory picture of the influence of substituting groups on the rate of reaction. In the first place, the majority of the experiments were made in light petroleum, in which the sodium alkyl-oxide was suspended, and accidental circumstances play a great part in determining the course of such reactions in heterogeneous systems. Further, the reactions were allowed to proceed almost to completion in many cases before observations were made, and therefore the results throw very little light on the influence of substitution on the reaction velocity. One of Bischoff's main objects was to find what substances were formed in the course of the reaction, and this was sufficiently secured by his method of experiment. A repetition of some of his observations, with due attention to the rate of reaction, would probably lead to interesting results.

Slator (*Trans.*, 1904, 85, 1286; 1905, 87, 482; this vol., 93) has made an extensive series of measurements on the rate of reaction between organic halogen compounds and sodium thiosulphate, and shows that for compounds of the same type the rate of the reaction generally diminishes with increasing complexity of the substituting group. The earlier experiments of Wislicenus, Menschutkin, and Hecht, Conrad and Brückner with other reagents also show that the activity of the halogens is diminished by substitution of alkyl groups for

hydrogen. This is evidently the typical behaviour, and corresponds with the results with sodium hydroxide described in the present paper. Quite a different order of activity is obtained when the rate of reaction between halogen compounds and silver nitrate is measured (Burke and Donnan, *Trans.*, 1904, 85, 555). This type of reaction will be discussed later, when the results of measurements now in progress are available, but the provisional results quoted in table X show that the order of activity of the bromo-fatty acids with silver nitrate is quite different from the typical one.

The results promise to throw some light on the so-called "Walden inversion," the investigation of which has recently been again undertaken by Fischer (*Ber.*, 1907, 40, 489) and by McKenzie (*Trans.*, 1908, 93, 811). Walden (*Ber.*, 1899, 32, 1848), in order to account for the different action of alkalis and of silver salts on the halogen derivatives of fatty acids, has suggested that such compounds as bromopropionic acid are dissociated to a considerable extent in solution with production of halogen ions, and that in the presence of alkalis direct exchange takes place between the halogen ions and the OH' ions. In the reaction between the halogen-fatty acids and silver nitrate, on the other hand, it is considered that complex addition compounds are formed which, after rearrangement, give rise to the final products.

The results described in the present series of papers, especially the fact that sodium bromide has practically no effect on the rate of displacement of bromine in α -bromopropionic acid by water, appear entirely to disprove Walden's theory that halogen ions are present in solutions of the free halogen-fatty acids. Even in the case of solutions of the sodium salts, it is very improbable that the anions give rise to halogen ions by ionisation, and the fact that the reaction between sodium bromoacetate and sodium hydroxide is bimolecular shows that in any case the rate at which halogen ions are formed is not the sole determining cause of the observed reaction velocity. The view of the mechanism of the reaction advocated in the present paper does not postulate an ionisation of the ordinary type, in which positive and negative ions are formed in equivalent amount, but the slow removal of a Br' ion, leaving a neutral molecule. On the other hand, there is no reason to doubt that the mechanism of the displacement of halogen by hydroxyl under the influence of alkali and of silver salts respectively is essentially different. The matter will be further discussed in connexion with the experiments on the reactions of silver salts with halogen-fatty acids now in progress.

In conclusion, I desire to express my thanks to the Directors of the Davy-Faraday Research Laboratory of the Royal Institution, where

part of the experimental work has been carried out, and also to Dr. Flürscheim, with whom I have had the advantage of discussing the subject matter of the paper.

CHEMICAL DEPARTMENT,
ST. MARY'S HOSPITAL MEDICAL SCHOOL, W.

CCIV.—*Ethyl Ether. Part I. The Influence of Water and Alcohol on its Boiling Point.*

By JOHN WADE, D.Sc., and HORACE FINNEMORE, B.Sc.

It is usually assumed that ether is pure when readily recognised impurities, such as alcohol, aldehyde, and hydrogen peroxide, have been eliminated by washing, and dissolved water has been removed by digestion with calcium chloride or quicklime, followed by sodium or phosphoric oxide. The boiling points given by modern workers are concordant: Schiff (*Annalen*, 1883, **220**, 232), Perkin (*Trans.*, 1884, **45**, 474), and Ramsay and Young (*Phil. Trans.*, 1887, **51**, 57) all agree on 34.6°. The discrepancies between the densities, however, are greater than can be attributed to experimental error. In the following table, which embodies the principal data, the reductions have been made by means of the coefficients of expansion determined by the respective authors, except with Perkin's number, for which a mean coefficient was used; Squibb's values have also been corrected for expansion of glass and for buoyancy. Squibb and Oudemans give values for several specimens, of which the extremes have been taken:

Authority.	Drying agent.	Densities.		
		Original.	Reduced to 0°/4°.	Reduced to 15°/15°.
Kopp (<i>Ann. Phys. Chem.</i> , 1847, 72 , 228)	Calcium chloride	0.72895 6.9°/4°	0.73658	0.72058
Perkin (<i>loc. cit.</i> , 1884).....	Phosphoric oxide	0.72008 15°/15°	0.73625	(0.72008)
Squibb (<i>Ephemeris</i> , 1885, 2 , 592)	Calcium chloride	0.71928 15°/4°	0.73633	0.72004
		{ 0.71908 15°/4°	0.73612	0.71984
		{ 0.73128 4°/4°	0.73611	0.71982
Oudemans (<i>Rec. trav. chim.</i> , 1885, 4 , 269).....	Lime and sodium	0.73600 0°/4°	(0.73600)	0.71983
		0.73586 0°/4°	(0.73586)	0.71969
Pierre (<i>Ann. Chim. Phys.</i> , 1845, [iii], 15 , 260)	Calcium chloride	0.73591 0°/4°	(0.73591)	0.71975

Accurate fractionation of various specimens of ether, which had been carefully purified by the processes employed above, showed

that in no case was a really homogeneous product obtained; every specimen was resolvable into constituents having varying boiling points and densities. It was hoped at first that it would be possible eventually to isolate the pure substance in this manner in accordance with previous experience; and, indeed, in the majority of instances, principal fractions were obtained which agreed in boiling point to 0.01° . The want of uniformity, however, in the densities of these fractions—which, in ordinary circumstances, would certainly have been found to be pure—showed that excellent agreement in boiling point might exist concurrently with appreciable variations in composition, and that it was doubtful whether finality had been reached.

Indications afforded by the earlier fractionations rendered it probable that this curious disagreement between the two constants was due to the formation of a physical mixture, or mixtures, analogous to the mixtures of constant boiling point isolated by Young and Fortey from alcohol (Trans., 1902, **81**, 717), and by the present authors from chloroform (*ibid.*, 1904, **85**, 1938). The behaviour of artificial mixtures of ether with water and alcohol was therefore investigated. It was eventually found that, on the one hand, a small proportion of water appreciably depresses the boiling point of ether, owing to the formation of a definite binary mixture; and, on the other hand, that a small proportion of alcohol, although not forming a definite mixture of this class, clings to ether with remarkable persistence, and appreciably raises its boiling point.

Unless, therefore, all the alcohol, and all but a trace of the water are first removed, it follows that it is impossible to obtain pure ether by any process of fractional distillation; and that constancy in its boiling point, especially as determined in the course of ordinary rectification, may be due merely to the mutual cancelling of these two opposing factors, and cannot, as is usually assumed, be accepted as conclusive evidence of the purity of this substance.

I.—*Examination of Ether Purified by Existing Processes.*

The experiments described below were made with commercial "pure" ether, prepared from rectified spirit and pure sulphuric acid. The sp. grs. of the various specimens (0.7213 , 0.7222 , 0.7214 , 0.7219 at $15^{\circ}/15^{\circ}$) fell within the customary limits; water and appreciable quantities of alcohol were invariably present.

The various products, after treatment as described, were fractionated with the usual precautions through a Young evaporator

column having eight sections.* The boiling points, which were checked by reference to standard thermometers, are expressed on the hydrogen scale, and reduced by means of Ramsay and Young's vapour pressure data (*loc. cit.*) to 760 mm. at 0° and Lat. 45°. The sp. grs. were determined at t°/t° in a large (40 c.c.) pycnometer of Ostwald-Sprengel pattern, and corrected to vacuum. They were reduced to 15°/15° by means of the dilatation constants of Pierre and Oudemans, and are correct to one or two units in the fifth place.

The individuality of a fraction, such as is afforded by a very efficient still-head, is indicated by the relative constancy of its boiling point, and is conveniently measured by the ratio of its weight (Δw) to the increment of temperature (Δt). This ratio rises to a maximum as the boiling point of each individual (whether chemical or physical) is reached, after which, except at the end of a series, it falls again to a minimum. When maxima are very close together, as in the present work, and the member of higher boiling point is in large excess, the temperature of the lower maximum is invariably raised, sometimes to such an extent as altogether to obliterate it. To enable different fractionations to be compared, the weight is reduced to a percentage of the total quantity (W) treated. In the following tables, the ratio $100\Delta w/W\Delta t$ is indicated by the symbol Δ .

(a) *Simple Desiccation: Calcium Chloride, Lime, Sodium, Phosphoric Oxide, Calcium.*

i. Commercial pure ether (500 grams) was shaken with powdered, recently fused calcium chloride (40 grams) at intervals for six days, when crystals of the hydrated salt became visible. A portion (125 grams) was poured off and fractionated:

B. p.	Weight.	Δ .	B. p.	Weight.	Δ .
33·1 — 34·39°	8·4	5	34·45 — 34·49°	32·7	665
34·39	10·5	840	34·49	23·0	1840
34·39 — 34·43	20·8	420	Residue	12·2	—
34·43 — 34·45	11·7	470	Loss	5·7	—

There were two maxima, and therefore two constituents. The head fraction became turbid when mixed with carbon disulphide, and therefore contained water. This was confirmed by the densities. The sp. gr. of the original ether was 0·72137, which, after the desiccation, fell to 0·72036. The sp. gr. of the second, third, and

* Much trouble was caused at the outset by excessive loss through evaporation, even with an efficient condenser the heavy vapour pouring steadily out of the mouth of the receiver. It was sufficiently checked ultimately by keeping both condenser and receiver nearly at 0°.

fourth fractions (which were mixed in order to fill the pyknometer) was 0.72024, and that of the fifth and sixth 0.72019. The accumulation of water in the head fraction, the formation of two maxima, and the progressively falling densities, indicate the presence of a binary mixture of ether and water, having a boiling point not much below that of pure ether.

Further drying still further lowered the density. A portion of the partly dried product, sp. gr. 0.72036 (150 grams), was kept over sodium shavings (2.4 grams) for five days, and then rectified from the metal. The sp. gr. fell to 0.72020. To another portion (185 grams), excess of phosphoric oxide was added (19 grams required). After rectification, the sp. gr. fell to 0.72001. These specimens were not fractionated at the time, and when examined later had deteriorated.

ii. As the action of calcium chloride is slow, some commercial ether (300 grams) was digested with sodium shavings until gas ceased to be evolved. Next day it was rectified over phosphoric oxide. The sp. gr. was 0.72015. A portion (160 grams) was fractionated:

B. p.	Weight.	Δ .	B. p.	Weight.	Δ .
33.2—34.35°	3.6	2	34.52—34.56	19.0	300
34.35—34.42	6.0	55	34.56—34.58	16.7	520
34.42—34.44	7.6	240	34.58	16.0	1000
34.44—34.46	15.4	480	34.58—34.60	9.7	300
34.46—34.50	16.0	250	Residue	10.0	—
34.50—34.52°	20.8	650	Loss	20.0	—

There were three distinct maxima, and apparently three constituents. The first and second coincided with those obtained after drying with calcium chloride, but the third, and most important, was at a higher temperature. The additional maximum seemed to indicate a second binary mixture, possibly ether-alcohol. This is discussed later (p. 1850). The fractions were too close for accurate determination of density, but the separation was obviously inferior to that effected with the calcium chloride product (i).

iii. Metallic calcium was comparatively ineffective as a desiccating agent. Some commercial ether (160 grams) was boiled with calcium raspings (5 grams) for four hours, and then kept for a week at the ordinary temperature. As a slow action was still proceeding, the experiment was then stopped. The sp. gr. of the rectified product was 0.72024.

(b) *Oxidation and Desiccation.*

i. Some commercial ether (150 grams) was shaken with a 4 per cent. solution of chromic acid (50 c.c.) and finally boiled for an hour (compare Dunstan and Dymond, *Trans.*, 1890, 57, 574;

Lassar-Cohn, *Annalen*, 1895, **284**, 226). Aldehyde having been removed by digestion with silver oxide, the product was dried with calcium chloride. A portion (92 grams) was fractionated:

B. p.	Weight.	Δ .	B. p.	Weight.	Δ .
32.6—34.25°	3.1	2	34.45—34.49°	13.9	380
34.25—34.39	9.5	74	34.49—34.51	12.5	680
34.39—34.43	8.9	245	34.51—34.53	10.9	590
34.43—34.45	10.1	550	Residue and loss	23.1	—

The two maxima corresponded fairly with those of the calcium chloride product, but were much less definite. There was much dissolved water in the head fraction, and an appreciable amount of aldehyde. The fractions were not large enough for accurate determination of density.

ii. Slightly alkaline permanganate, under suitable conditions, oxidises alcohol directly to acetic acid, or perhaps oxalic acid. It avoids the formation of aldehyde, and oxidises this if already present; it is thus well adapted for the purification of ether (François, *J. Pharm. Chim.*, 1897, [vi], **5**, 521). Some commercial ether (150 grams) was shaken with aqueous permanganate (2.5 grams in 50 c.c., with a little alkali hydroxide), with which it was finally boiled for half an hour. The rectified product was dried with calcium chloride, and fractionated (118 grams):

B. p.	Weight.	Δ .	B. p.	Weight.	Δ .
32.65—34.24°	3.0	2	34.48—34.50°	12.0	510
34.24—34.40	11.1	59	34.50	16.1	1370
34.40—34.42	11.4	480	34.50—34.52	17.7	750
34.42—34.44	14.4	610	Residue	7.0	—
34.44—34.48	13.9	290	Loss	11.4	—

The second maximum was sharper than with chromic acid. There was no aldehyde in the head fraction, but a considerable amount of water.

iii. The best oxidation process examined was a modification of the preceding method, due to Dr. Fierz, which was kindly communicated to the authors by Dr. M. O. Forster, in whose laboratory it has been employed for some time past. Commercial ether (200 grams) was digested with a mixture of powdered potassium permanganate (5 grams) and potassium hydroxide (5 grams) for a week at the ordinary temperature, the bottle being occasionally shaken. It was then poured off and rectified. The sp. gr. was 0.72020; another specimen subsequently prepared in the same manner had sp. gr. 0.72021. A portion (181 grams) was fractionated:

B. p.	Weight.	Δ .	B. p.	Weight.	Δ .
33.2—34.39°	9.7	4	34.45—34.47°	11.4	315
34.39—34.41	12.4	340	34.47—34.51	22.0	305
34.41—34.43	11.8	330	34.51	88.4	4890
34.43—34.45	10.9	300	Residue and loss	14.4	—

The first maximum was the least sharp of any yet observed, and was evidently on the point of obliteration. The second was much the sharpest, and represented nearly half the total product; the sp. gr. of this fraction was 0.72006. The head fraction contained a little water, but aldehyde was absent.

(c) *Exhaustive Washing and Desiccation.*

Lieben (*Annalen, Suppl.*, 1871, 7, 218) recommends removing alcohol by shaking with small quantities of water until the iodoform test gives a negative result; he found 20 or 30 washings necessary. Ramsay and Young (*loc. cit.*) found that 50 washings were needed. Squibb (*loc. cit.*) employed relatively large quantities of water, with which the ether was agitated mechanically for considerable periods; he found 6 washings sufficient, in the course of which, however, one-third of the ether was lost. Oudemans (*loc. cit.*), using Lieben's method, stopped after 15 or 20 washings. To test this method, some commercial ether (700 grams) was shaken for fifteen minutes at a time with successive small quantities (50 c.c.) of water. After the 16th washing, when the weight had been reduced to 570 grams, the iodoform test ceased to give a definite indication of the presence of alcohol in the wash-water.*

i. Part of the washed ether (250 grams) was dried by Oudemans' method (*loc. cit.*). It was first digested with fresh quicklime (50 grams, from marble) for two days in a well-filled flask, and then rectified from the lime. The first and last portions of the distillate having been rejected, the remainder was then digested with sodium shavings (2.4 grams), with which there was a slight, although immediate, action. Next day, the ether (183 grams) was rectified from the sodium; as the sp. gr. was then 0.72013, further examination was unnecessary.

ii. The remainder of the washed ether (307 grams) was digested with calcium chloride for two days, and then rectified from phosphoric oxide (37 grams). The product (240 grams) was fractionated; its sp. gr. was 0.71999:

B. p.	Weight.	Δ.	B. p.	Weight.	Δ.
33.58—34.38°	4.2	2	34.48—34.49°	24.0	1000
34.38—34.42	10.1	105	34.49	173.0	7200
34.42—34.48	12.3	85	Residue and loss	16.4	—

The first maximum had now practically disappeared. The second indicated a highly purified product, representing nearly three-fourths of the whole; its sp. gr. was 0.71994. This was the best result obtained with ether purified by existing processes.

* The ether employed in this work had already been washed to a certain extent in the course of manufacture.

(d) Summary of Results with Ether Purified by Existing Processes.

No.	Treatment.	Differential of best fractions.	B. p.	Sp. gr.	
				Whole.	Best fraction.
b i	Chromic acid and calcium chloride...	680	34·51°	—	—
a ii	Sodium and phosphoric oxide	1000	34·58	—	—
b ii	Aqueous permanganate and calcium chloride	1370	34·50	—	—
a i	Calcium chloride only	1840	34·49	0·72036	0·72019
a iii	Metallic calcium	—	—	0·72024	—
b iii	Solid permanganate and alkali	4890	34·51	0·72020	0·72006
a i	Calcium chloride and sodium	—	—	0·72020	—
c i	Washing; lime and sodium	—	—	0·72013	—
a i	Calcium chloride and phosphoric oxide	—	—	0·72001	—
c i	Washing; calcium chloride and phos- phoric oxide	7200	34·49	0·71999	0·71994

From these results, it was clear that the boiling point of pure ether is very near 34·50°, and its sp. gr. probably below 0·71994. As was to be expected, the sp. grs. decreased as the differentials increased; but there was no evidence of finality. A considerably lower sp. gr. was, in fact, obtained at a later stage by methods which are still under investigation. The influence of water and alcohol were obviously very important factors in the purification, and needed examination before further progress could be made.

II.—*Isolation of Binary Mixtures of Ether and Water: Investigation of Supposed Binary Mixture with Alcohol: Absence of Ternary Mixture.*

(a) Binary Aqueous Mixture.

i. *Ether and Excess of Water.*—Commercial ether (130 grams) was fractionated in presence of water (50 grams):

B. p.	Weight.	Δ.	B. p.	Weight.	Δ.
33·7 —34·10°	5·3	10	34·19—100°	small	—
34·10—34·19	14·1	120	Residue	50·5	—
34·19	96·2	7400	Loss	13·2	—

Practically three-fourths formed a homogeneous product of lower boiling point than pure ether. This was quite clear when first collected (sp. gr. 0·7245), but there were numerous small drops of water in the fractionating column, and after a time minute drops also appeared in the distillate. When the layer of ether in the still had disappeared, the boiling point rose at once to 100°, and

the distillation was stopped. The whole distillate was now dried roughly with calcium chloride, and fractionated (100 grams):

B. p.	Weight.	Δ.	B. p.	Weight.	Δ.
33·9 —34·16°	3·4	13	34·36—34·40°	18·4	460
34·16—34·30	14·9	105	34·40—34·46	15·3	255
34·30—34·36	10·7	180	34·46—34·50	16·2	405
			Residue and loss	21·1	—

The product closely approximated to those previously obtained from purified ether. There were two distinct maxima, and the head and second fractions showed appreciable amounts of water when tested with carbon disulphide.

In order to define the boiling point accurately, and ascertain the composition of the aqueous mixture, purified ether, b. p. 34·49°, sp. gr. 0·72002 (50 grams), was fractionated in presence of water (50 grams):

B. p.	Weight.	Δ.
33·8—34·15°	7·6	44
34·15	35·0	7000
35·0—100	small	—

The boiling point was here exceedingly sharp, and became constant practically as soon as equilibrium was established. At 15°, the ether was just about saturated with water, the percentage of which, calculated from the sp. gr., was 1·3.* The loss by evaporation was too uncertain to allow of analysis by distillation.

* The sp. gr. of highly purified ether, sp. gr. 0·71982, saturated with water at various temperatures, was determined hydrostatically by means of a weighted glass sinker displacing about 30 c.c. The proportion of water was then calculated, allowing for contraction.

Temperature	20°	18°	16°	15°	14°	12°	10°
Sp. gr. at t°	0·7193	0·7214	0·7234	0·7244	0·7254	0·7272	0·7290
Weight of water dissolved by 1 gram of ether	0·013	0·013	0·013	0·013	0·0125	0·011	0·009

The contraction was determined from the sp. gr. of solutions of known composition, which were prepared by agitating ether in a well-stoppered bottle with water introduced in a small bulb.

- I. 0·6057 water in 50·31 ether, sp. gr. 0·71984, gave solution sp. gr. 0·72415.
 II. 0·4042 ,, 50·92 ,, ,, 0·72000, ,, ,, ,, 0·72423.
 I. Sp. gr. calculated 0·72228; contraction, 0·26 per cent.
 II. ,, ,, 0·72205; ,, 0·30 ,,

The values given by various authorities for the solubility of water in ether are very discordant, possibly owing to the difficulty of purifying the ether—the solubility is greatly increased by even a very small quantity of alcohol; it is significant, however, that if the important correction for contraction be omitted, the values calculated from the above data become 0·023 from 20° to 15°, and 0·019 at

ii. *Water and Excess of Ether.*—The complete separation of two constituents, boiling within 0.35° of one another, is impracticable, and previous experience had shown that in such cases the constituent of higher boiling point can only be isolated when present in very large excess. Separation of pure ether in this manner was eventually effected from an imperfectly dried product, from which it is believed that every impurity but water had been removed. Some highly purified ether, which, when fully dried with phosphoric oxide, had b. p. 34.51° , Δ 8500, and sp. gr. 0.71982, was treated, after roughly drying with calcium chloride, with an amount of phosphoric oxide known to be insufficient. It was then fractionated (300 grams):

B. p.	Weight.	Δ .	B. p.	Weight.	Δ
34.35—34.42°	8.8	4	34.46—34.48°	11.0	180
34.42—34.49	21.6	100	34.48—34.51	22.8	250
34.44—34.46	23.6	390	34.51—34.52	194.0	6470
			Residue and loss	18.2	—

There were two maxima, which corresponded closely with those of the ether purified by Fierz's method (p. 1846). The sp. gr. of the third fraction (with part of the second) was 0.72012, and that of the fourth and fifth 0.72011. The sp. gr. of the main fraction was 0.71986, or very nearly that of the completely dried product. Ether, sp. gr. 0.72012, contains 0.14 per cent. of water. The elimination even of this small proportion of water as a more volatile constituent completes the proof of the formation of a binary mixture of ether and water of minimum boiling point.

Ether therefore forms with water a binary mixture, which boils at 34.15° , and contains approximately 1.3 per cent. of water.

(b) *Supposed Binary Mixture with Alcohol.*

i. *Ether with much Alcohol.*—Some of the ether, sp. gr. 0.72013, which had been dried with sodium and phosphoric oxide (p. 1845), was fractionated with an equal weight of 99.8 per cent. alcohol (50 grams):

B. p.	Weight.	Δ .	B. p.	Weight.	Δ .
34.62—34.73°	5.7	50	78.05—78.21°	6.5	40
34.73	9.6	960	78.21—78.23	9.2	460
34.73—34.81	8.2	100	78.23—78.25	10.9	545
34.81—35.0	7.2	40	78.25—78.27	15.0	750
35.0 —78.05	1.7	0.04	Residue and loss	26.0	—

10°. The following are the amounts of water stated to be dissolved by 1 gram of ether at the respective temperatures:

Klobbie (<i>Zeitsch. physikal. Chem.</i> , 1897, 24, 615) ...	0.012—0.0127 at 20°
Schuncke (<i>ibid.</i> , 1894, 14, 334)	{ 0.02702 ,, 10
	{ 0.0272 ,, 20
Napier (<i>Bull. Soc. chim.</i> , 1878, [ii], 29, 122) ..	0.0278 ,, 12
Herz (<i>Ber.</i> , 1899, 31, 2671)	0.0407 ,, 22

The elevation of boiling point originally noticed with this specimen ($34\cdot68^\circ$) was now still more decided; absolutely nothing passed over until well above the boiling point of pure ether. The temperature rose slowly until most of the ether had distilled, and then very rapidly to the boiling point of alcohol. The sp. gr. of the main ether fraction was $0\cdot7211$, corresponding with about 1·6 per cent. of alcohol. There was no indication of other maxima, but this was possibly due to the large amount of alcohol in the still (compare ethyl acetate, Wade, Trans., 1905, **87**, 1664). Repetition with rather different proportions gave a substantially identical result, the main ether fraction boiling at $34\cdot75^\circ$, and the alcohol fraction at $78\cdot31^\circ$. In both cases the head fraction remained clear when mixed with excess of carbon disulphide; but water may nevertheless have been present, as a very little alcohol greatly increases its solubility in this mixture.

ii. *Ether with little Alcohol*.—Some highly purified ether, sp. gr. $0\cdot71986$ (150 grams), was fractionated with a little nearly anhydrous alcohol (1·5 grams):

B. p.	Weight.	Δ .	B. p.	Weight.	Δ .
$34\cdot35-34\cdot53^\circ$	10·6	40	$34\cdot65^\circ$	23·9	1580
$34\cdot53-34\cdot59$	7·7	80	$34\cdot65-34\cdot67$	26·3	870
$34\cdot59-34\cdot63$	26·7	440	$34\cdot67-34\cdot69$	13·7	450
$34\cdot63-34\cdot65$	11·8	390	$34\cdot69-34\cdot77$	15·9	130
			Residue and loss	14·9	—

There were two maxima, both above the boiling point of pure ether and corresponding fairly with the two upper maxima of the abnormal ether (p. 1845). The sp. gr. of each maximal fraction was $0\cdot7201$, but after the second maximum the sp. grs. increased rapidly; that of the tail fraction was $0\cdot7207$. The sp. gr. of the residue was $0\cdot7374$; evidently little of the alcohol had passed over.

The collected distillates were refractionated (128·0 grams), excluding the residue:

B. p.	Weight.	Δ .	B. p.	Weight.	Δ .
$34\cdot0-34\cdot47^\circ$	9·1	14	$34\cdot50-34\cdot52^\circ$	9·9	380
$34\cdot47-34\cdot49$	10·1	395	$34\cdot52-34\cdot53$	77·1	6030
$34\cdot49-34\cdot50$	11·2	875	Residue and loss	10·8	—

The maxima, which were now much more definite, had fallen very near the boiling point of ether, although the upper one was still distinctly high. The sp. gr. of this fraction was $0\cdot72019$. The sp. gr. of the residue was $0\cdot7235$. Most of the alcohol which had passed over in the first fractionation had therefore been eliminated.

Repetition with suitable variations gave substantially the same results. There was no sign of a third maximum except on one occasion, when a little water was accidentally introduced in preparing for a refractionation. Highly purified ether, sp. gr. $0\cdot71982$

(150 grams), on fractionation with a little 99·8 per cent. alcohol (1·5 grams) had given maxima at 34·53° (Δ 385) and 34·63° (Δ 3510; sp. gr. 0·7202). The sp. gr. of the residue was 0·7323. The collected distillates were now refractionated as stated (114·0 grams; perhaps 0·2 gram of water):

B. p.	Weight.	Δ .	B. p.	Weight.	Δ .
33·9 — 34·47°	9·2	14	34·52°	34·7	3020
34·47	9·3	815	34·52—34·53	15·6	1370
34·47—34·49	4·2	185	34·53—34·57	4·0	90
34·49	11·7	1025	Residue	10·0	—
34·49—34·52	11·7	340	Loss	3·6	—

There were here undoubtedly three maxima. The sp. gr. of the two head fractions was 0·7207; of the fourth and fifth (with part of the sixth), 0·72047; of the sixth, 0·72049; and of the residue, 0·7215. The water had evidently passed into the head fractions; the alcohol, as before, was in process of elimination. This normal differentiation, taken in conjunction with the extreme closeness of the three maxima, rendered it probable that the middle maximum was a false one—a shadow of the first, as it were—due to elevation of boiling point by the alcohol in the still as the concentration increased.

iii. *Ether with very little Alcohol.*—It was thus probable that the lower maximum, which appears so persistently in the preceding fractionations, was merely due to a trace of water, and that ether does not form a binary mixture with alcohol. Direct proof of this could only be furnished by fractionating anhydrous ether with anhydrous alcohol in a dry atmosphere. Practically decisive evidence was obtained, however, by fractionating imperfectly dried ether, sp. gr. 0·72001 (150 grams), with a very little anhydrous alcohol (0·5 gram):

B. p.	Weight.	Δ .	B. p.	Weight.	Δ .
33·5 — 34·47°	14·0	10	34·49°	65·1	4340
34·47—34·49	21·6	720	Residue	39·0	—
			Loss	10·8	—

The sp. gr. of the first two fractions was 0·72018; of the main fraction, 0·71996; and of the residue, 0·72106. The boiling point and sp. gr. of the main fraction were those of fairly good ether, distinctly better than the original. The amount of water required to raise the sp. gr. of 35·6 grams of ether from 0·72001 to 0·72018 is 0·028 gram. The amount which must be withdrawn in order to lower the sp. gr. of 65·1 grams of ether from 0·72001 to 0·71996 is 0·017 gram; the difference is not greater than would be accounted for by the residual hygroscopic moisture adhering to the glass of the apparatus. The amount of alcohol required to raise the sp. gr.

of 39.0 grams of ether from 0.72001 to 0.72106 is approximately 0.6 gram, and is fairly well accounted for by the 0.5 gram added.

It may be concluded that ether does not form a binary mixture with alcohol, although its boiling point, and that of the binary mixture with water, is markedly raised even by small quantities of this impurity.

(c) *Absence of a Ternary Mixture.*

So far as the authors are aware, there is no instance of the formation of a ternary mixture without the accompanying formation, under appropriate conditions, of the three possible binary mixtures. This does not seem a priori impossible, however. At any rate, the point is doubtful, and, although the occurrence of the third maximum in the foregoing fractionations had been fairly satisfactorily accounted for, it was still possible that the lowest might be due to the formation of a mixture of this class.

Commercial ether (70 grams) was fractionated with alcohol (20 grams) and water (10 grams), which formed a clear solution with it at ordinary temperatures:

B. p.	Weight.	Δ.	B. p.	Weight.	Δ.
34.06—34.16°	5.0	50	34.34°	29.6	2960
34.16—34.24	14.1	175	Residue	29.0	—
34.24—34.34	10.3	100	Loss	12.0	—

There were here two maxima. These might conceivably have indicated a ternary mixture, followed by the binary aqueous mixture, but that this was impossible in presence of the very large excess of alcohol. The alternative was that the upper maximum was a duplicate or shadow (p. 1852) of the lower, due to the rapidly increasing concentration of the alcohol in the still. Repetition with a larger proportion of ether (160 grams) gave a much sharper lower maximum (b. p. 34.19°, Δ 1460), and a lower boiling point for the upper maximum (34.23°, Δ 2950); the two maxima were evidently verging on coincidence. And on fractionating ether (50 grams) with much alcohol (36 grams) and little water (0.5 gram), only two maxima were obtained: ether, b. p. 34.18°, Δ 1280; and alcohol, b. p. 78.12—78.18°, Δ 212. The two lower maxima had coincided.

As the lowest maximum in each case was above the boiling point of the binary aqueous mixture (34.15°), it was now practically certain that it was due to the latter, the boiling point being raised, as in the case of dry ether, by the excess of alcohol in the still. This was finally established by refractionating the collective distil-

lates from the first fractionation (58.0 grams) with water (20.0 grams):

B. p.	Weight.	Δ.
34.0—34.14°	5.5	68
34.15	42.8	7380
Residue	19.5	—
Loss	10.2	—

There was now only one maximum, identical with that of the binary aqueous mixture. A ternary mixture would not have been resolved by thus distilling with water.

Ether therefore does not form a ternary mixture with alcohol and water.

As ether forms a binary mixture with water, which boils with characteristic constancy 0.35° lower than the pure substance, and contains enough water to saturate it at the ordinary temperature, it follows that when moist ether is fractionated it will commence to pass over at a rather lower temperature than pure ether; and that unless all but a trace of the water is first removed, the pure substance cannot be obtained from it by any process of distillation. Further, as the boiling points both of ether and of its binary mixture are raised by the presence of alcohol, the formation of a maximum above the true boiling point from any particular specimen is strong presumptive evidence of the presence of alcohol in that specimen.

It may be concluded that, in order to obtain pure ether, it is necessary, first, that the alcohol should be completely eliminated, and then all but the merest trace of water; from such a product a good yield of anhydrous ether should then be procurable by accurate fractionation. From these data, the authors have succeeded in devising processes which, as will have been noticed from examples mentioned incidentally in the preceding pages, have already furnished ether of a higher order of purity than any of the specimens which they have treated by the older methods. As in the case of chloroform, however, the problem is complicated by the peculiar instability of the highly purified substance; this has necessitated yet further investigation, the results of which it is hoped to communicate in the near future.

CCV.—*The Colouring Matters of the Flowers of Hibiscus sabdariffa and Thespasia lampas.*

By ARTHUR GEORGE PERKIN.

Hibiscus sabdariffa.

THE *Hibiscus sabdariffa* (Rozelle or Patwa), or Red Sorrel of the West Indies, is a small shrub which grows from three to four feet high, and is widely cultivated throughout the hotter parts of India and Ceylon. There is a considerable demand for this plant among the natives of India, for in the North-West Provinces it is grown as a food plant, and similarly in the Punjaub it is cultivated for the sake of its succulent acid calyces. The stems yield the Rozelle hemp of commerce, and this is obtained by retting the twigs as soon as the plant is in flower (Watts, *Dict. of Economic Products of India*, IV, 242). According to Burkill (*Agricultural Ledger, Calcutta*, 1908, No. 2, 13), the *Hibiscus sabdariffa* has fleshy, red calyces and pale yellow flowers. The yellow flowers are just capable of dyeing yellow, but are not used at all in India for this purpose; on the other hand, the red calyces are employed for dyeing in a very obscure degree in two remote parts of the country. Their use in Chutiá Nágpur was made known by the Rev. A. Campbell, and their use among the Shans by Leveson.

The sample employed in this investigation was kindly sent me by the authorities of the Imperial Institute, and these flowers included the stalk, epicalyx, calyx, and corolla. Unfortunately, however, the material had considerably deteriorated during transport, for on arrival most of the flowers had suffered decoloration, and the red colouring matter was now practically absent.

EXPERIMENTAL.

The material was digested with ten times its weight of boiling water for six hours, the mixture filtered, and the residue well pressed. The deep brown extract was treated with sulphuric acid to the extent of 2 per cent., which caused it to become red coloured, and the solution digested at the boiling point for two hours in order to hydrolyse the glucosides present. As the liquid, on cooling, had not deposited any colouring matter, it was extracted with a large volume of ether—a very troublesome operation, because the mixture emulsified, and the ethereal extract did not completely separate until after several hours. The latter was removed,

repeatedly washed with water, evaporated to dryness, and the small quantity of brownish-yellow residue which thus remained was digested with boiling water, and the next day the crude yellow colouring matter was collected (the filtrate A being reserved for further examination). The yield of this product was poor, as 500 grams of the flowers gave, on the average, only 1.8 grams of the crude substance, and during the operations described below this suffered a very considerable diminution.

For purification, the semi-crystalline substance was dissolved in a large volume of boiling absolute alcohol, and the solution partly evaporated. A small quantity of crystals thus separated, which were collected and washed with alcohol (B), and a further trace of this compound was usually deposited on distilling off more of the alcohol. The alcoholic solution was now treated while hot with a little boiling water, and the yellow product which separated on cooling was collected and recrystallised from dilute alcohol.

As the complete purification of this compound, the main colouring matter derived from the flowers, by further crystallisation was not feasible, it was acetylated by a short digestion with boiling acetic anhydride, to which a few drops of pyridine had been added (Proc., 1908, **24**, 150), and the product isolated by precipitation with water was crystallised from alcohol until colourless.

As thus obtained, it melted at 222—224°, and on analysis gave C=57.25; H=4.23 per cent. To hydrolyse this product, it was dissolved in acetic acid, a little sulphuric acid was added, the solution boiled, and subsequently treated with water. The pale yellow needles which separated gave, on analysis:

Found, C=57.51; H=3.49.

$C_{16}H_{12}O_8$ requires C=57.83; H=3.61 per cent.

It was, however, subsequently observed that when this apparently pure acetyl compound was recrystallised twice from acetic acid containing a little alcohol, its melting point rose to 229—230°, and this, on analysis, gave slightly lower figures:

Found, C=56.88; H=4.19.

$C_{15}H_4O_8(C_2H_3O)_6$ requires C=56.84; H=3.86 per cent.

By hydrolysis in the manner above-described, the amount of colouring matter thus produced also agreed well with this formula:

Found, $C_{15}H_{10}O_8$ = 55.93; 55.85.

$C_{27}H_{22}O_{14}$ requires $C_{15}H_{10}O_8$ = 55.79 per cent.

The free colouring matter, dried at 160°, gave the following result:

Found, C=56.60, 56.40; H=3.37, 3.28.

$C_{15}H_{10}O_8$ requires C=56.60; H=3.14 per cent.

It consisted of pale yellow needles, which, after some time, developed a green tint, and appeared to melt between 295° and 300° , but the exact point was obscured by the darkening of the tube. It dissolves in concentrated alkalis to form orange-red solutions, and these, when diluted with water, become green coloured, and finally dull brown. If a suspension of the colouring matter in water is treated with one drop of the alkali, the green coloration is at once produced, and this, by oxidation with the air, develops on the surface a transient blue tint. With alcoholic lead acetate, it gives a deep red precipitate, which, on boiling, becomes brown, and alcoholic ferric chloride produces a deep olive-green liquid. Mineral acids, in the presence of acetic acid, gave in the usual way orange-red, crystalline compounds, but owing to the scarcity of material, sufficient of these could not be produced for analysis.

By fusion with alkali, for which but a very small quantity of substance was available, a colourless, crystalline product was obtained. This melted at 194 — 196° , gave with aqueous lead acetate a colourless precipitate, with ferric chloride a deep green coloration, and was thus evidently protocatechuic acid.

Dyeing experiments with this colouring matter, employing mordanted wool, gave the following shades:

Aluminium.	Tin.	Chromium.	Iron.
Pale orange-brown.	Orange-red.	Dull brown.	Deep dull olive.

In the presence of chalk, the shade obtained with the aluminium mordant is olive-yellow, a result which is probably due to a partial oxidation either of the free colouring matter in the dye-bath, or of the lake which is subsequently produced.

These results suggested that this colouring matter of the flowers of the *Hibiscus sabdariffa* was gossypetin, a substance which exists in the flowers of the Indian cotton plant, *Gossypium herbaceum* (Trans., 1899, 75, 825), and a comparison of the two products subsequently showed that this was the case. To gossypetin the formula $C_{16}H_{12}O_8$ was previously assigned, and the melting point of its hexa-acetyl derivative was stated to be 222 — 224° . The results given above, however, indicate that the true formula is more probably $C_{15}H_{10}O_8$, and that the original preparation from the cotton flowers, of which very little was available for experiment, was most likely contaminated with a trace of an analogous colouring matter, containing a higher percentage of carbon, and, in fact, there is evidence that such a compound also exists in minute quantity in these *Hibiscus* flowers. To determine, if possible, the identity of this substance, an examination of the mother liquors obtained during the purification of acetylgossypetin was carried out, and as a result a trace of a slightly more soluble acetyl

derivative was isolated, which melted almost entirely at 190—194°, although it was evidently not quite pure. It is thus probable that in addition to gossypetin a small quantity of quercetin is also present in these flowers, and that the complete separation of these substances is only effected when the admixture of their acetyl derivatives is frequently crystallised from acetic acid. Finally, analyses of gossypetin obtained from Egyptian cotton flowers, the examination of which is now in progress, have given results also in harmony with the formula $C_{15}H_{10}O_8$.

Gossypetin is thus apparently isomeric with myricetin (Trans., 1902, **81**, 203), and there is a considerable resemblance between these two substances as regards the colorations produced from them by means of dilute alkali. On the other hand, hexa-acetylmyricetin melts at 211—212°, and by fusion with alkali gives gallic acid.

The aqueous filtrate A (p. 1856) obtained during the isolation of the crude colouring matter from these flowers was extracted with ether, which removed a small quantity of a readily soluble compound. This, after repeated crystallisation from water, formed colourless needles, melting at 194—196°, which gave, with ferric chloride, a green coloration, and consisted of protocatechuic acid. It is possible that this compound may not exist in the fresh flowers, and may be derived from protocatechualdehyde, for it is known that the odour of certain flowers is due to the presence of the latter substance.

As regards the sparingly soluble colouring matter (B) (p. 1856) isolated with the gossypetin, and removed from it by fractional crystallisation, the very small amount obtained admitted only of a very cursory examination of its properties. It consisted of pale yellow, glistening leaflets, which melted at about 340° with decomposition, but the exact point could not be observed, owing to the darkening of the tube. It does not contain a methoxy-group, does not appear to form crystalline acid compounds with mineral acids, and dissolves in alkalis with a yellow colour. On acetylation, it gives a colourless, very sparingly soluble acetyl derivative, melting at 238—239°, and it dyes mordanted calico. The analysis of this compound, which appears to be an hitherto unknown colouring matter, and for which the name *hibiscetin* is proposed, was carried out, but the result is reserved, in the hope that it may be possible later to obtain a large quantity of the flowers in a state of good preservation, so that sufficient of this compound can be prepared for a more thorough examination.

A search for hibiscetin in the sepals of the better known *Hibiscus rosa sinensis*, for a supply of which I am much indebted to Mr. Lawrence Balls, of the Khedivial Agricultural Society at

Cairo, was carried out with a negative result. This material contained only the merest trace of yellow colouring matter, which it was not possible to characterise, and in the flowers' calyces this was, moreover, also practically absent.

Thespesia lampas.

The *Thespesia lampas* is a small bush common to the tropical jungles of India, Burma, and Ceylon. In Watt's *Dictionary of the Economic Products of India*, there is no mention of the use of this plant as a dyestuff, but, on the other hand, the capsules and flowers of the allied *Thespesia populnea* are stated to give a yellow dye, and this point has been corroborated by the late Sir Thomas Wardle (*Report on the Dyes and Tans of India*). For the material employed I am indebted to the authorities of the Imperial Institute: this consisted entirely of the yellow sepals of the plant, which in general appearance closely resembled those of the *Gossypium herbaceum*. The quantity available for examination was small, and had suffered partial decoloration.

The method employed for the isolation of the yellow colouring matter, which is present in these flowers in the form of glucoside, was identical with that found serviceable in the case of the *Hibiscus sabdariffa*. Two hundred and fifty grams of the material gave 1.5 grams of the crude dyestuff, and this was purified by crystallisation from dilute alcohol, followed by conversion into its acetyl compound. The latter consisted of long, colourless needles, melting at 191—194°:

Found, C=58.66; H=4.12.

$C_{15}H_5O_7(C_2H_3O)_5$ requires C=58.59; H=3.90 per cent.

This compound possessed all the properties of acetylquercetin, and the reactions of the free colouring matter, obtained as glistening, yellow needles, also indicated without doubt that it consisted of quercetin.

Curiously enough, the aqueous filtrate obtained during the isolation of the quercetin was found to contain protocathechuic acid, which, as shown above, was also obtained from the *Hibiscus sabdariffa*. It was identified by means of its melting point, 194—196°, and its characteristic reaction with ferric chloride. Dyeing experiments with these flowers, employing mordanted woollen cloth, gave fairly good shades, which do not, however, call for special comment. They were in no way superior to the better known Indian natural yellow dyestuffs, although locally they might perhaps find useful employment. On the other hand, the shades produced by the flowers of the *Hibiscus sabdariffa* were of a

much poorer character, but this may possibly be accounted for by the fact already alluded to, that the sample was of inferior quality, and in no way equal to the freshly gathered material.

CLOTHWORKERS' RESEARCH LABORATORY,
THE UNIVERSITY,
LEEDS.

CCVI.—*Dynamics of the Reaction between Iodine and Acetone.*

By HARRY MEDFORTH DAWSON and MAY SYBIL LESLIE, M.Sc.

IN the course of some measurements of the molecular solution volume of iodine in various solvents, it was found that widely divergent and abnormally low values were obtained in acetone solution. For a freshly prepared solution the molecular solution volume was much larger than that for a solution of the same concentration which had been prepared for some hours. This observation relative to the change in the volume of the dissolved iodine was evidently connected with certain variations found in the conductivity of acetone solutions of iodine. These variations, originally observed during some experiments on the formation of polyiodides of the alkali metals and substituted ammonium bases in acetone, were not only obtained in the case of a pure iodine solution, but also in that of solutions containing iodide and iodine. In all cases the conductivity increased very considerably, and at the ordinary temperature the change was soon completed. The actual observations for a 0.1 molar solution of iodine may be quoted. The specific conductivity at 18° of a solution made up as quickly as possible was 4.5×10^{-4} mho; at the end of half an hour the conductivity had increased to 57.0×10^{-4} , and remained constant at this value. At 0° the velocity of the change, which could be readily followed by the position of the minimum on the bridge wire of the conductivity circuit, was much smaller, and about four hours were required before the equilibrium condition was attained. The change in conductivity and in the volume of the dissolved iodine was evidently due to the substituting action of the iodine on the acetone, for the final solution was found to be strongly acid, and the iodine titre had undergone considerable diminution. For a solution of given concentration a definite end-point appeared to be reached, indicating that the reaction involved is reversible.

With the object of elucidating its nature, the reaction between iodine and acetone has been investigated dynamically under varying conditions. To reduce the velocity the reacting substances were dissolved in various solvents, of which water was the one chiefly used. In the case of aqueous solutions, the dependence of the velocity on the acetone and iodine concentrations and on the acidity was determined. For convenience, the data obtained for aqueous solutions will be considered first.

In all the experiments to be referred to, the conditions were such that the acetone was in large excess relatively to the iodine, so that the concentration of the acetone was practically constant throughout the course of the reaction. If hydrogen ions are present in moderate concentration, the reaction proceeds with conveniently measurable velocity at the ordinary temperature. In the absence of added acid, the initial velocity of the reaction is very small, but since hydrogen iodide is formed as the reaction proceeds, the velocity of the change gradually increases. When the conditions are so chosen that the original concentration of the hydrogen ions is not appreciably altered in consequence of the gradual formation of hydrogen iodide, the experiments show that the iodine disappears at a rate which remains constant from the commencement until near the end of the change. The velocity constant appears to be proportional to the concentration of the acetone in the aqueous solution, and also to the concentration of the acid.

The experiments from which these conclusions are drawn were made at a temperature of 20° , which was maintained constant to about 0.05° . Since iodine is only slightly soluble in dilute aqueous solutions of acetone, it was found necessary to add potassium iodide in small quantity in order to obtain iodine solutions of sufficiently large concentration. A known volume of freshly prepared solution, contained in a stoppered flask in the thermostat, was acidified by the addition of a definite volume of standard acid, and from time to time measured portions of the solution were run into excess of a dilute solution of sodium hydrogen carbonate, and the iodine determined by means of sodium thiosulphate. If the acid solution is not neutralised in this way before titration, the iodine cannot be estimated, for the interaction of the added sodium thiosulphate with the iodine results in the formation of increasing quantities of iodide, and therefore of hydriodic acid, and this leads to a reversion of the original reaction and the liberation of iodine. In these circumstances, the blue colour of the solution returns slowly after it has been discharged, and a definite end-point is not reached until an amount of thiosulphate, approximately

equivalent to the iodine originally present in the solution, has been added.

In table A, the data are recorded which were obtained in experiments in which the acetone concentration was varied between wide limits, and, further, those which show the influence of the acid concentration on the velocity of the reaction. As previously indicated, the iodine disappears at a constant rate in accordance with the equation:

$$-\frac{dx}{dt} = k \quad \dots \quad (1),$$

where x is the concentration of iodine after time t . If a represents the original concentration of the iodine, we obtain for the integral equation:

$$x = a - kt \quad \dots \quad (2),$$

Under t are given the time intervals from the commencement of the reaction in minutes, whilst x_1 and x_2 represent respectively the experimental iodine concentrations (mols. per litre) and those calculated from equation (2) by the aid of constants which are indicated at the foot of each series of data. In all the solutions examined, the concentration of the potassium iodide was 0.02 mol. per litre:

TABLE A.

EXPERIMENT 1.			EXPERIMENT 2.		
Acetone 5 grams per litre; 0.1N-H ₂ SO ₄ .			Acetone 15.5 grams per litre; 0.1N-H ₂ SO ₄ .		
<i>t</i> .	$x_1 \cdot 10^4$.	$x_2 \cdot 10^4$.	<i>t</i> .	$x_1 \cdot 10^4$.	$x_2 \cdot 10^4$.
90	74.4	75.0	30	70.7	71.4
180	67.15	67.9	92	56.7	57.2
285	59.7	59.8	191	34.7	34.7
360	54.3	53.9	236	24.4	24.4
			261	18.9	18.7
			309	7.7	7.8
	$x_2 = 0.0082 - 0.0000078t$.			$x_2 = 0.00782 - 0.0000228t$.	
EXPERIMENT 3.			EXPERIMENT 4.		
Acetone 60 grams per litre; 0.1N-H ₂ SO ₄ .			Acetone 120 grams per litre; 0.1N-H ₂ SO ₄ .		
<i>t</i> .	$x_1 \cdot 10^4$.	$x_2 \cdot 10^4$.	<i>t</i> .	$x_1 \cdot 10^4$.	$x_2 \cdot 10^4$.
23	60.6	61.8	13.5	56.5	58.5
48	40.1	39.8	25.0	38.5	38.5
77	14.2	14.2	44.5	5.8	4.6
	$x_2 = 0.0082 - 0.000088t$.			$x_2 = 0.0082 - 0.000174t$.	
EXPERIMENT 5.			EXPERIMENT 6.		
Acetone 5 grams per litre; 1.0N-H ₂ SO ₄ .			Acetone 15.5 grams per litre; 0.5N-H ₂ SO ₄ .		
<i>t</i> .	$x_1 \cdot 10^4$.	$x_2 \cdot 10^4$.	<i>t</i> .	$x_1 \cdot 10^4$.	$x_2 \cdot 10^4$.
29	57.5	58.2	10.5	66.0	66.0
50	41.0	41.0	26.5	47.0	47.5
81	19.9	15.6	36.5	36.0	35.9
	$x_2 = 0.0082 - 0.000082t$.		56.5	13.5	12.7
				$x_2 = 0.00782 - 0.000116t$.	

From the agreement between the values of x_1 and x_2 , it is clear that the iodine disappears at a constant rate. This is certainly true for the major part of the reaction, although experiments in which the reaction was followed to near the end indicate that the velocity diminishes considerably when the transformation is nearly complete. For a given acetone solution this effect appears to increase with the concentration of the acid present; it is probably connected with the reversibility of the reaction, an increase in the acid concentration resulting in the liberation of a larger proportion of hydriodic acid from the iodide present.

A comparison of the values of the velocity constant k in experiments 1 to 4 shows that these are almost exactly proportional to the concentration of the acetone. If the constant for the solution containing 15.5 grams of acetone per litre is taken as basis, the constants calculated on the assumption of proportionality are, for the solutions containing 5, 60, and 120 grams per litre, respectively 0.00000735, 0.000088, and 0.000176, whereas the corresponding experimental values are 0.0000078, 0.000088, and 0.000174.

In a similar way, a comparison of the values of k for experiments 1 and 5 and for experiments 2 and 6, shows that the velocity of the reaction is almost exactly proportional to the concentration of the sulphuric acid. If the activity of the acid is due to the hydrogen ions, it follows from this that the catalytic effect of the ions increases more rapidly than corresponds with the increase in their concentration. A similar relationship has been found in other reactions, in which acids act as catalysts.

In table B, the data obtained in experiments with hydrochloric and acetic acids are recorded; these experiments are comparable with experiment 6 of table A, in which a solution containing an equivalent amount of sulphuric acid was examined.

TABLE B.

Acetone 15.5 grams per litre ; 0.5 <i>N</i> -HCl.			Acetone 15.5 grams per litre ; 0.5 <i>N</i> -CH ₃ CO ₂ H.		
<i>t</i> .	$x_1 \cdot 10^4$.	$x_2 \cdot 10^4$.	<i>t</i> .	$x_1 \cdot 10^4$.	$x_2 \cdot 10^4$.
8.5	66.0	67.1	120	76.5	76.45
21.5	49.5	50.0	1100	62.6	62.0
39.5	26.5	26.5	1530	55.7	55.7
48.0	16.8	15.3	2640	39.2	39.4
$x_2 = 0.00782 - 0.000131t$.			$x_2 = 0.00782 - 0.00000147t$.		

From these data, it follows that the velocity constants for comparable solutions containing hydrochloric, sulphuric, and acetic acids respectively in 0.5*N*-concentration are in the ratio 1.31, 1.16, 0.0147. These numbers are approximately in the ratio of the degrees of ionisation of the acids, and indicate that the observed

catalytic influence is primarily due to the hydrogen ions. If we assume that the catalytic effect in dilute acid solutions is proportional to the concentration of the hydrogen ions, then from the value of the constant for 0.5*N*-hydrochloric acid, which may be regarded as ionised to the extent of 82 per cent., we obtain for the rate of disappearance of iodine in an acidified aqueous solution of acetone at 20°:

$$-\frac{dx}{dt} = k = 0.0012 \alpha c_1 c_2 \text{ mols. litre/minute,}$$

c_1 being the concentration of the acid in equivalents per litre, α its degree of ionisation, and c_2 the concentration of the acetone in mols. per litre.

Action of Iodine on Acetone in Neutral Solution.

In the absence of acid, the rate at which iodine reacts with acetone is very small. Since, however, hydrogen iodide appears as one of the products of the reaction, it follows that the reaction velocity should increase as the reaction proceeds, in consequence of the gradually increasing concentration of the hydrogen ions. That this is the case is shown by the following experiment.

The quantity of potassium iodide required to give a 0.005 molar solution was weighed out into a 500 c.c. flask, and in this was placed a small quantity of water and excess of iodine. After shaking until no more iodine dissolved, the solution was diluted, and, after the addition of 25 c.c. of acetone, made up to 500 c.c. The clear solution was then syphoned off from the undissolved iodine, and placed in a thermostat at 20°. After measured time intervals, the iodine concentration was determined by removing 50 c.c. of the solution to a flask containing about 50 c.c. of water, 5 c.c. of a 0.2*N*-sodium hydrogen carbonate solution, and about 0.5 gram of potassium iodide. Without the addition of potassium iodide, a satisfactory end-point could not be obtained on titrating with 0.01*N*-thiosulphate solution. This phenomenon, which nullified the first attempts to determine the progress of the reaction in the absence of foreign acid, has not as yet received an explanation. Table C contains the data for the above experiment. From the values of the mean velocity during the successive time intervals, it is evident that the velocity increases as the amount of iodine in the solution diminishes. This auto-catalytic effect will, of course, be also exhibited in solutions to which a foreign acid has been added, provided that the ratio of the concentration of the acid to that of the iodine at the commencement is not too large:

TABLE C.

Time.	Concentration of iodine, mols. per litre.	Mean velocity, mols. per litre per hour.
0	0.002088	
24 hours	0.001892	8.2×10^{-6}
46 "	0.001482	18.6×10^{-6}
65 "	0.000596	46.6×10^{-6}

Influence of Temperature on the Rate of Change.

With the object of ascertaining the influence of temperature on the rate of the reaction, comparative measurements were made at 20° and 30°. For this purpose, a solution was used containing 8.83 grams of acetone and 0.2 gram-equivalent of sulphuric acid per litre. In order to obtain the iodine in a sufficiently large concentration, potassium iodide was added to give a 0.02 molar solution. The results of these measurements are recorded in exactly the same way as in table A:

TABLE D.

Temperature = 20°.			Temperature = 30°.		
<i>t.</i>	$x_1 \cdot 10^4.$	$x_2 \cdot 10^4.$	<i>t.</i>	$x_1 \cdot 10^4.$	$x_2 \cdot 10^4.$
29	73.5	72.4	24	61.75	61.4
70	60.75	61.55	55	37.0	37.2
92	55.55	55.7	77	20.0	20.1
112	51.25	50.4	97.5	5.6	4.1
138	44.0	43.55			
	$x_2 = 0.00801 - 0.0000265t.$			$x_2 = 0.00801 - 0.000078t.$	

It is evident from this table that the reaction proceeds with constant velocity at 30° in the same way as at 20°, and that for a rise of 10° the velocity increases in the ratio $78/26.5 = 2.95$. The reaction has therefore a temperature-coefficient which may be considered to be normal.

Action of Iodine on Acetone in Non-aqueous Solvents.

When liquids other than water are used to dilute the acetone, with the object of reducing its active mass, and thereby diminishing the velocity of the change, the phenomena which are met with differ very greatly from those observed in the case of aqueous solutions of acetone. As the result of preliminary experiments with solutions of acetone in carbon tetrachloride, methyl alcohol, methyl acetate, benzene, and nitrobenzene, it was found that in these cases the action of the iodine on the acetone is much less complete as compared with the action in a corresponding aqueous solution.

Equal quantities of iodine (0.50 gram) were weighed out into

a series of stoppered bottles, each containing 50 c.c. of one of the above solvents. After shaking to bring the iodine into solution, 5 c.c. of acetone were added to each bottle. The solutions were titrated at the end of twenty-four hours, in which time, as subsequent titrations showed, the reaction had reached a limit. The extent to which the reaction proceeds in the different solvents is shown by the percentage amounts of unchanged iodine, which were as follows: Carbon tetrachloride 72, benzene 72, methyl acetate 62, nitrobenzene 57, and methyl alcohol 47 per cent. The incompleteness of the reaction in these cases is in marked contrast to the behaviour of a corresponding aqueous solution. On making an exactly similar experiment with an aqueous acetone solution, which was made slightly acid so that the end-point would be reached more quickly, it was found that the percentage of unchanged iodine was only 0.35 per cent. From these results it is evident that in aqueous solution the reaction between iodine and acetone takes place much more completely than it does when other liquids are used as solvent media.

Another point of difference is presented by the much greater velocity with which the reaction appears to take place in the non-aqueous solvents as compared with the velocity in neutral aqueous solution. With the object of obtaining information relative to the influence of the solvent on the velocity of the change, comparative measurements were made in which carbon tetrachloride, benzene, nitrobenzene, and methyl alcohol were employed as solvents.

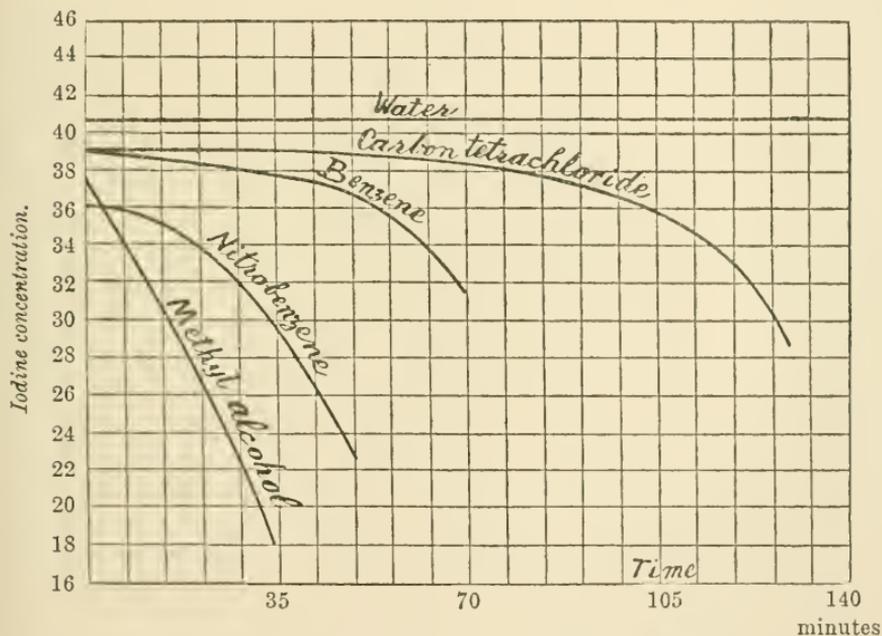
Solutions containing 10 per cent. by volume of acetone and about 0.04 mol. of iodine per litre were used. In the estimation of the unchanged iodine, the pipetted fraction of solution was run into a bottle containing about 250 c.c. of water and 10 c.c. of a 0.1*N*-sodium hydrogen carbonate solution, the contents being shaken violently after each addition of thiosulphate solution. The velocity of the reaction in the different solutions is deducible from the data in table E, which gives the number of c.c. of a 0.01*N*-sodium

TABLE E.

Carbon tetrachloride.		Benzene.		Nitrobenzene.		Methyl alcohol.	
Time.	C.c. of Na ₂ S ₂ O ₃ .	Time.	C.c. of Na ₂ S ₂ O ₃ .	Time.	C.c. of Na ₂ S ₂ O ₃ .	Time.	C.c. of Na ₂ S ₂ O ₃ .
0.0	39.0	0.0	—	0.0	36.1	0.0	37.6
64.5	38.6	4.5	38.9	8.0	35.6	7.0	33.9
81.5	37.8	24.0	38.2	26.5	32.5	17.5	28.75
94.5	36.75	44.0	37.2	38.0	27.75	25.5	24.0
107.0	35.65	57.5	35.4	49.0	23.2	34.5	18.7
119.0	33.25	68.5	31.6				
128.5	28.65						

thiosulphate solution required by 5 c.c. of the acetone-iodine solution after the time intervals indicated in minutes.

The differences caused by the variation of the solvent are best seen from the figure, in which curves are drawn through the points obtained by plotting iodine concentrations against the time intervals. From the relative positions of the curves, it is evident that the velocity of the reaction increases with the solvent in the order—carbon tetrachloride, benzene, nitrobenzene, methyl alcohol. In all cases, the slope of the curve towards the axis of abscissæ increases as the reaction progresses, which seems to indicate that there is an autocatalytic effect similar to that found in the case



Rate of action of iodine on acetone in different solvents.

of aqueous solutions. On the same diagram the behaviour of an aqueous solution containing the same amount of iodine would be represented by a straight line parallel to the abscissæ; in other words, the initial velocity of the reaction in neutral aqueous solution is so small that no measurable change in the iodine concentration takes place by the time the reaction in the other solvents has come to an end. The position of the water curve on the diagram is not what would have been anticipated on the basis of the results obtained with the other four solvents. From the order in which these arrange themselves, it might indeed be expected that the velocity in water would be greater than in methyl alcohol.

That it is so very much smaller is probably due to differences in the mechanism of the change in the different solvents.

The factors which influence the velocity of the reaction in the case of non-aqueous solutions have not been ascertained, and it is therefore not possible to discuss the mechanism of the reaction under these conditions. On the other hand, the experiments on aqueous solutions are sufficiently complete to show that the relationships involved in this case are practically the same as those found by Lapworth (*Trans.*, 1904, **85**, 30) for the action of bromine on acetone in aqueous solution. Furthermore, Lapworth's view that the reaction between halogen and acetone takes place in two stages appears to afford a simple explanation of the observed facts.

Since the rate at which the iodine disappears is independent of its concentration, the particular reaction which determines the observed velocity of change is one in which iodine is not directly involved. This reaction, according to Lapworth, is the transformation of the ketonic form of acetone into the enolic form, and this is accelerated by acids. In the second stage, the iodine reacts with the enolic acetone, and the velocity with which this takes place is relatively so large that this stage in the complete reaction is practically without influence on the rate at which the iodine disappears. This theory explains the observed fact that the velocity is unaltered by the addition of potassium iodide, even when the quantity added reduces the concentration of the free iodine, as a consequence of polyiodide formation, to about one-fiftieth of the concentration in the iodide free solution. It is also consistent with the observed proportionality between the velocity of the change and the acetone concentration, for the rate of formation of the enolic acetone must be proportional to the concentration of the ketonic form, and this is practically identical with the total acetone concentration.

If the isomeric change in question is the factor which determines the rate at which acetone is acted on by all the halogens, then the observed velocities should be the same for chlorine, bromine, and iodine under comparable conditions. Lapworth has shown that this is the case for bromine and chlorine, although chlorine was found to act more rapidly at the commencement of the reaction when the concentration of the halogen was greatest. To test the theory further, we have compared the velocities in the case of iodine and bromine. For this purpose, we determined the velocity in a solution containing 15.5 grams of acetone, 0.1 gram-equivalent of sulphuric acid, 0.02 mol. of potassium bromide, and 0.008 mol. of bromine per litre. This solution is strictly comparable with the

iodine solution of experiment 2, table A, for which the constant k is 0.0000228, whereas that found for the bromine solution is 0.0000260. Although perhaps a closer agreement between the two constants might have been expected, the extent of the deviation—about 6 per cent. from the mean value—cannot be considered large enough to invalidate the theory. It is probable that the observed difference is due to secondary factors, the nature of which might be put in evidence by a detailed comparison of the velocities of the two reactions.

Whilst the experimental data thus indicate that the mechanism of the reaction is the same for the different halogens, the behaviour of iodine is to some extent different, in that the reaction in certain circumstances is reversible. Although no attempt has been made in this paper to determine the exact nature of the equilibrium relationships, certain observations connected with the reversibility of the change may be recorded.

On passing hydrogen iodide into an acidified aqueous solution, from which the iodine originally present had almost completely disappeared, iodine was at once set free in considerable quantity. The same result was obtained when iodoacetone, prepared by the action of potassium iodide on chloroacetone (Scholl and Matthaiopoulos, *Ber.*, 1896, **29**, 1550), was dissolved in acetone and subjected to the action of hydrogen iodide.

Although these observations demonstrate the reversibility of the change, it should be noted that the reaction proceeds practically to completion under the conditions of the dynamic experiments in tables A to D. If, however, the quantity of iodine which is added to a given aqueous solution of acetone is increased, a gradually increasing proportion remains unchanged at the end of the reaction. In some qualitative experiments, it was found, for instance, that when a gram-molecule of acetone dissolved in a litre of water is brought in contact with 0.01 or 0.02 gram-molecule of iodine, the resulting solution is nearly colourless, whereas with 0.04 gram-molecule of iodine an appreciable proportion of the latter remains unacted on when the end-point is reached. These facts serve to emphasise the difference between aqueous and non-aqueous solutions in regard to the extent to which the reaction proceeds. In pure acetone the equilibrium relationships are similar to those in non-aqueous solutions, as may be seen from the fact that in a 0.02 molar solution the reaction comes to an end when about 45 per cent. of the iodine has been transformed. Taken in conjunction with the observation that the velocity of the reaction in neutral aqueous solution appears to be very much smaller than

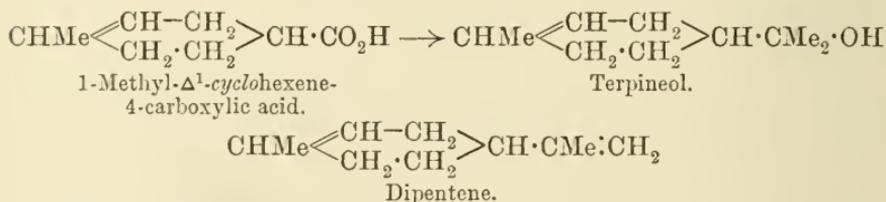
the velocity in non-aqueous solutions, the differences in behaviour suggest that the mechanism of the change in the two cases is different. It is hoped that further experiments may decide whether this is the case or not.

THE UNIVERSITY,
LEEDS.

CCVII.—*The Reduction of 4-Hydroxy-o-toluic Acid.*

By OSCAR BAUDISCH, GILBERT STANLEY HIBBERT, and
WILLIAM HENRY PERKIN, jun.

THE experiments on the synthesis of the terpenes which have been carried out in these laboratories during the last few years are based on the preparation, in the first instance, of an unsaturated acid, the ester of which, when treated with magnesium methyl iodide, yields the corresponding terpeneol, from which, by the action of dehydrating agents, the terpene is obtained in the usual manner. Thus, for example, terpeneol and dipentene were synthesised according to the scheme:



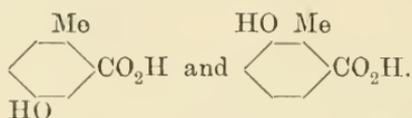
Several other unsaturated acids have already been synthesised and converted successfully into the corresponding terpeneols and terpenes by a similar series of reactions. In continuing these researches, the object which has more particularly been kept in view has been the synthesis of unknown members of the ortho- and meta-series of the terpene group, but the great difficulty throughout has been the problem of discovering methods for the preparation of the requisite unsaturated acids, especially in quantities sufficient for subsequent investigation. The three communications now submitted contain an account of the first portion of an investigation undertaken with the object of preparing a new series of methylcyclohexenecarboxylic acids (tetrahydrotoluic acids) for the purpose of subsequent use in the synthesis of terpenes and their derivatives. The processes employed in all the cases are similar, and may therefore be well illustrated by a single example.

In the present communication, the starting point is 4-hydroxy-o-

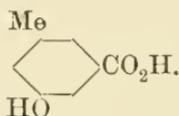
aromatic series. There is thus reason to believe that the only aromatic hydroxy-acids which can be reduced to the corresponding hexahydro-derivatives by sodium and alcohol are those in which the hydroxy-group and carboxy-group occupy the meta-position with respect to one another.

If this be true, it is easily seen that in the toluic acid series only four acids are available for reduction, namely:

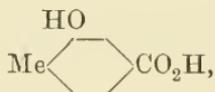
I. From *o*-toluic acid, the two acids,



II. From *m*-toluic acid, the acid of the formula



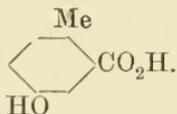
III. From *p*-toluic acid, the acid



and the reduction of this acid by alcohol and sodium has already been the subject of a careful investigation (Meldrum and Perkin, *Trans.*, 1908, **93**, 1417).

The experiments described in this and the two following communications show that, as was to be expected, all the above *m*-hydroxy-acids may be reduced with comparative ease by sodium and alcohol, and a detailed description is given of the various hydroxy-acids which are obtained in this way. Experiments on the conversion of these hydroxy-acids into the corresponding unsaturated acids and into the terpeneols and terpenes have been commenced, and will form the subject of future communications.

The present communication deals with the reduction of *4*-hydroxy-*o*-toluic acid,

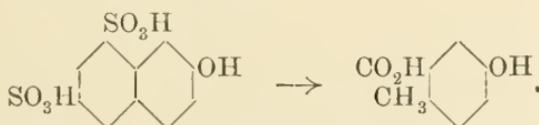


This acid seems to have been first prepared by Jacobsen (*Ber.*, 1881, **14**, 41), who obtained it from 4-sulphamino-*o*-toluic acid by fusion with potassium hydroxide, and subsequently (*Ber.*, 1884, **17**, 163) by treating 4-amino-*o*-toluic acid with nitrous acid, and he states that it melts at 172°. More recently a number of patents have been taken out which show that this acid may be obtained from certain derivatives of

naphthalene by a remarkable decomposition due to the action of fused alkali. Kalle & Co. (D.R.-P. 91201, Friedländer, *Fortschritte der Teerfarbenfabrikation*, IV, 148) show that it is formed from naphthalene-1 : 3 : 7-trisulphonic acid, 1-naphthylamine-3 : 7-disulphonic acid, and 8-amino-2-naphthol-6-sulphonic acid by fusion with potassium hydroxide at 260°. The Farbwerke vorm. Meister, Lucius & Brüning (D.R.-P. 81281 and 81333, Friedländer, *ibid.*, IV, 149—150) obtained the same acid from 2-naphthylamine 6 : 8-disulphonic acid or 2-naphthol-6 : 8-disulphonic acid (*G*-acid) by fusion with sodium hydroxide at 260—320°. All these naphthalene derivatives contain the substituent groups in the positions marked by asterisks in the formula,



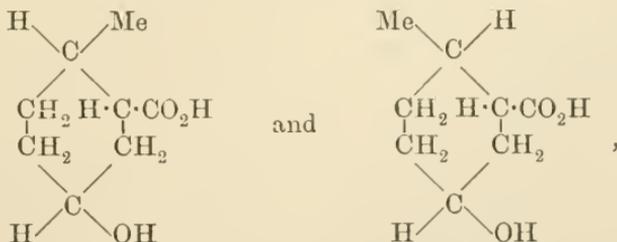
and the remarkable process of reduction and oxidation caused by the fusion with alkali hydroxide at the high temperature employed may be illustrated in the case of *G*-acid :



The yield obtained from *G*-acid is remarkably good, and most of the 4-hydroxy-*o*-toluic acid required for this investigation was prepared from *G*-acid by fusion with sodium hydroxide under the conditions described on p. 1875. When quite pure it melts at 183°, and not at 172° as stated by Jacobsen (*loc. cit.*).

4-Hydroxy-*o*-toluic acid is reduced by sodium and alcohol with some difficulty, and is converted into a mixture of hydroxy-acids, from which all the four possible isomerides (two *cis*- and two *trans*-) have been isolated in a pure condition.

The two *cis*-1-methylcyclohexan-4-ol-2-carboxylic acids,

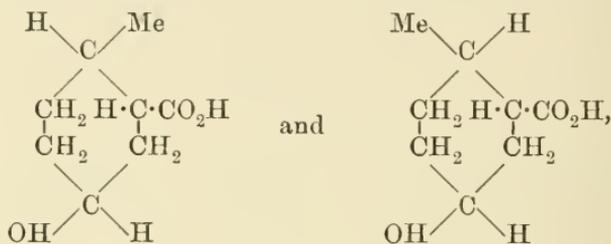


melt at 191° and 126—128° respectively, and, as it has not been found possible to determine with which of the above formulæ each of these acids corresponds, they have been named *cis*-(A) (m. p. 191°) and *cis*-(B) (m. p. 126—128°). The *cis*-(A) acid decomposes at its melting

point into steam and an oil, but, unfortunately, owing to the small amount of material available, we have not been able to determine the nature of the lactone or unsaturated acid which is produced as the result of this decomposition. The *cis*-(B) acid decomposes at about 160° into steam and a lactone, which distils at 130—135°/20 mm., and is converted into the *cis*-(B) acid on dissolution in alkali hydroxide.

Both the *cis*-(A) and the *cis*-(B) acids yield the corresponding *bromo*-acids when treated with fuming hydrobromic acid, but whereas *cis*-(A)-*bromo*-1-methylcyclohexane-2-carboxylic acid is crystalline and melts at 103—105°, the corresponding *cis*-(B)-*bromo*-acid is a syrup.

The two *trans*-1-methylcyclohexan-4-ol-2-carboxylic acids,



melt at 163—165° and 122—123° respectively, and differ from the *cis*-acids in the fact that they do not decompose with elimination of steam until about 220°. In this case, also, we have no evidence to show with which of the above formulæ each of these *trans*-acids corresponds, and we have therefore named the acid of melting point 163—165° *trans*-(A), and the acid of melting point 122—123°, *trans*-(B).

These two acids are converted into the corresponding *bromo*-acids when they are heated with hydrobromic acid, and the esters of these acids, as also the esters of the *cis*-*bromo*-acids, yield, on heating with diethylaniline, unsaturated esters, which are at present under investigation.

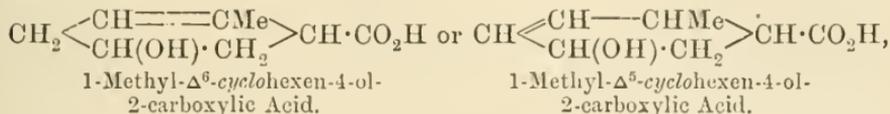
During the reduction of 4-hydroxy-*o*-toluic acid with sodium and alcohol, there is always formed, sometimes in considerable quantities, an unsaturated acid, C₈H₁₂O₃, which readily yields a beautifully crystalline lactone (m. p. 44°) at the ordinary temperature, and this passes over when the product of reduction is distilled in a current of steam.

There can be little doubt that this unsaturated acid is an intermediate step in the reduction of 4-hydroxy-*o*-toluic acid, and is converted, by the further action of the sodium and alcohol, into the 1-methylcyclohexan-4-ol-2-carboxylic acids.

The behaviour of the acid towards permanganate shows that it is unsaturated, and this is confirmed by the fact that the lactone reacts with fuming hydrobromic acid with formation of a *dibromo*-acid,

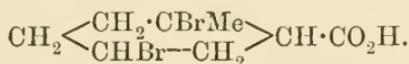
$C_8H_{12}O_2Br_2$, a crystalline substance (m. p. 158—160°), which is decomposed by cold sodium carbonate with elimination of carbon dioxide and separation of a heavy neutral oil containing bromine.

The ease with which the hydroxy-acid, $C_8H_{12}O_3$, is converted into the lactone seems to indicate clearly that it is a γ -hydroxy-acid possessing one of the formulæ :

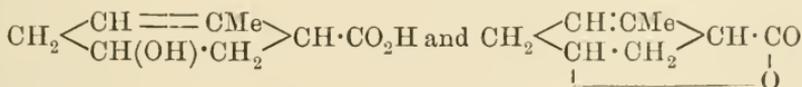


and, of these, the former is to be preferred.

The fact that the dibromo-derivative, $C_8H_{12}O_2Br_2$, readily loses carbon dioxide and yields a neutral brominated oil when it is treated with sodium carbonate at the ordinary temperature, recalls the similar behaviour observed in the case of the β -halogen derivatives of phenylpropionic acid, $C_6H_5 \cdot CHX \cdot CH_2 \cdot CO_2H$, which are decomposed by cold sodium carbonate with elimination of carbon dioxide and formation of styrene. It is therefore probable that one of the bromine atoms in the bromo-derivative, $C_8H_{12}O_2Br_2$, occupies the β -position in relation to the carboxyl group, and, as the second bromine atom, owing to the acid, $C_8H_{12}O_3$, being derived from 4-hydroxy-*o*-toluic acid, must occupy the 4-position, the constitution of the dibromo-derivative is, in all probability,



We assume, therefore, that the hydroxy-acid, $C_8H_{12}O_3$, and its lactone have the constitutions represented by the formulæ :



respectively.

Preparation and Reduction of 4-Hydroxy-o-toluic Acid.

In preparing this acid, sodium 2-naphthol-6 : 8-disulphonate,* in quantities of 1.5 kilos., was fused with sodium hydroxide (3 kilos.) and water (3 kilos.) in an autoclave of 6 litres capacity at 260—280° for twelve hours. The product was diluted with half its volume of water, acidified with hydrochloric acid, and the crude 4-hydroxy-*o*-toluic acid collected and washed with a little water. The mass was then dissolved in a slight excess of hot sodium carbonate, filtered, and again acidified, when the acid separated in almost colourless crystals,

* We wish to express our thanks to Messrs. Cassella & Co. for kindly supplying us with a large quantity of this salt.

and, after once crystallising from water, it was quite pure and melted at 183°. The yield obtained was about 380 grams.

The reduction was carried out under the following conditions: The pure acid (100 grams) was dissolved in pure ethyl alcohol* (2 litres) in a 10-litre flask connected with a very long and very efficient reflux condenser, to the end of which a condenser sloping downwards was attached. The sodium (300 grams), in pieces as large as could conveniently be put into the flask, was introduced all at once, when the alcohol soon began to boil and was carried over in quantities by the vigorous evolution of hydrogen. Most of it condensed and ran back into the flask, and the remainder was condensed by the downward condenser and collected in a large flask kept cool by running water. When the action had moderated, the distilled alcohol was poured back, and, as soon as the sodium showed signs of solidifying, the flask was shaken vigorously and the action allowed to proceed, if necessary with the addition of small quantities of hot alcohol, until the sodium had almost disappeared.

A mixture of alcohol and water was then cautiously added, and then enough water to dissolve the sodium salt; the solution was then allowed to cool, nearly neutralised by the addition of hydrochloric acid, and the alcohol distilled off from a salt-solution bath. The residue was acidified with excess of hydrochloric acid, when a syrup separated, which was extracted three times with ether, the ethereal solution washed with a little water, very thoroughly dried, the ether distilled off, and the residue again reduced under the same conditions as before. The acid from the second reduction was now distilled in steam, in order to remove as much as possible of an unsaturated lactone (A, p. 1881). The residue was again extracted, and the crude mixture of hydroxy-acids esterified by digesting, in quantities of 100 grams, with absolute alcohol (300 c.c.) and sulphuric acid (20 c.c.) on a reflux apparatus for six hours. The product was diluted with water, extracted with ether, the ethereal solution well washed with water and dilute sodium carbonate, evaporated, and the residue fractionated under 15 mm. pressure, when a large quantity of a viscid oil (60—70 grams) passed over below 180°, leaving a dark residue in the flask, which was not further examined. After two further fractionations, the bulk of the oil (55 grams) distilled at 150—160°/15 mm., and this was mixed with a moderately concentrated solution of potassium hydroxide (35 grams) in methyl alcohol and left at the

* Experience has shown that it is a matter of great importance, in reductions of this kind, that the alcohol shall be as anhydrous as possible, as even the presence of half a per cent. of water retards reduction in a quite unexpected manner and sometimes entirely prevents it. The "absolute" alcohol employed in these experiments was distilled over calcium before use.

ordinary temperature overnight. The product was diluted with water, unhydrolysed ester (*A*, 8 grams) extracted with ether, the aqueous solution saturated with carbon dioxide, evaporated until free from methyl alcohol, acidified, and extracted four times with pure ether (*B*) and then a further eight times on the machine (*C*).

The extract, *B*, was evaporated and the viscid oil placed over sulphuric acid for some weeks; the semi-solid mass was then left in contact with porous porcelain until the oily impurity had been completely removed. When the colourless mass was systematically crystallised from water, it was separated with some considerable difficulty into two acids, namely, *trans*(*A*)- and *cis*(*A*)-1-methylcyclohexan-4-ol-2-carboxylic acids, melting at 163—165° and 190—191° respectively.

The ethereal extract (*C*) yielded, on evaporation, a syrup (5 grams), which rapidly crystallised, and, after contact with porous porcelain, the colourless mass separated from water in bunches of colourless prisms, melting at 190—191°, and consisting of pure *cis*(*A*)-1-methylcyclohexan-4-ol-2-carboxylic acid. The ester (*A*), which had escaped hydrolysis in the cold, was hydrolysed by digesting with excess of methyl-alcoholic potassium hydroxide on the water-bath, and yielded a viscid syrup, which gradually crystallised. After remaining in contact with porous porcelain, the residue was several times recrystallised from ether, when a small quantity of an acid was obtained, which melted at 190—191° and proved to be *cis*(*A*)-acid.

The mother liquors were evaporated, and the semi-solid mass again transferred to porous porcelain until quite dry and free from oil.

When the residue was systematically crystallised from ether, it yielded, besides a little *cis*(*A*)-acid, a relatively large quantity of an acid, which separated from ether in thin crusts, like paper, and from water in hard, chalky crusts. This acid melts at 122—123°, and has been named *trans*(*B*)-1-methylcyclohexan-4-ol-2-carboxylic acid. This partial hydrolysis experiment, which has been several times repeated, indicates that of the three acids mentioned, the ester of the *trans*(*A*)-acid is the most readily hydrolysed in the cold, and that of the esters of the *cis*(*A*)- and *trans*(*B*)-acids, the latter is hydrolysed with more difficulty than the former.

trans(*A*)-1-Methylcyclohexan-4-ol-2-carboxylic acid melts at 163—165° without decomposition, and its decomposing point appears to be approximately 220—225°. It is sparingly soluble in ether, but apparently more readily so than the *cis*(*A*)-acid, and separates from this solvent in hard, glistening crusts:

0.1386 gave 0.3080 CO₂ and 0.1140 H₂O. C = 60.8; H = 9.1.

0.1518 „ 0.3388 CO₂ „ 0.1232 H₂O. C = 60.8; H = 9.0.

C₈H₁₄O₃ requires C = 60.8; H = 8.8 per cent.

The basicity, determined by titration with *N*/10-sodium hydroxide, gave the following result : 0.2062 neutralised 0.0521 NaOH, whereas this amount of a monobasic acid, $C_8H_{14}O_3$, should neutralise 0.0522 NaOH.

This acid dissolves in hydrobromic acid (saturated at 0°), and the solution remains clear for many hours, but, when heated on the water-bath, it clouds, and in a short time an oily layer separates on the surface of the hydrobromic acid. After the addition of water, the heavy oil was extracted with ether, the ethereal solution washed, well dried, and carefully evaporated, and, after remaining for two hours over sulphuric acid in a vacuum desiccator, the syrup yielded, on analysis, numbers which showed that it was nearly pure *trans*(A)-4-bromo-1-methylcyclohexane-2-carboxylic acid :

0.1787 gave 0.1482 AgBr. Br = 35.2.

$C_8H_{13}O_2Br$ requires Br = 36.2 per cent.

When the *trans*(A)-hydroxy-acid (4.3 grams) was oxidised by potassium dichromate (2.8 grams), sulphuric acid (5 grams), and water (50 c.c.), a considerable quantity of unchanged acid was recovered, but no trace of keto-acid could be isolated.

trans(B)-1-1-Methylcyclohexan-4-ol-2-carboxylic acid melts at 122—123° :

0.1216 gave 0.2712 CO_2 and 0.0984 H_2O . C = 60.8 ; H = 8.9.

$C_8H_{14}O_3$ requires C = 60.8 ; H = 8.8 per cent.

It is rather sparingly soluble in ether, from which it separates in curious, characteristic, brittle crusts, like paper or egg shell.

From water, in which it is readily soluble, it separates in hard, chalky crusts. When heated in a capillary tube, no decomposition is observed until about 195°, when gas is very slowly disengaged, and even at 215° the decomposition is not rapid. The melting point of this acid (123°) is practically the same as that of the *cis*-B-acid (p. 1880), but when equal quantities of the two acids are mixed, the mixture softens at 90° and is almost melted at 105°.

cis(A)-1-Methylcyclohexan-4-ol-2-carboxylic acid melts at 190—121° with decomposition, and, if rather slowly heated, it decomposes below this temperature :

0.1140 gave 0.2530 CO_2 and 0.0930 H_2O . C = 60.5 ; H = 9.0.

$C_8H_{14}O_3$ requires C = 60.8 ; H = 8.8 per cent.

On titration with *N*/10-sodium hydroxide, 0.2071 neutralised 0.0524 NaOH, whereas this amount of a monobasic acid, $C_8H_{14}O_3$, should neutralise 0.0524 NaOH. This acid is very sparingly soluble in cold dry ether, but dissolves much more readily in the boiling solvent, and, if the solution is concentrated, the acid separates after some time as a crust of small, glistening prisms. It dissolves moderately readily

in hot water, and crystallises, on cooling, in beautiful, glistening bunches of prisms. The finely powdered acid dissolves readily in hydrobromic acid (saturated at 0°), and, after several hours, stellate groups of crystals appear. These were collected, drained on porous porcelain, and left over solid potassium hydroxide in a vacuum desiccator until dry, but, owing to its being rather unstable, no attempt was made to recrystallise the small amount of substance at our disposal :

0.0890 gave 0.0765 AgBr. Br = 36.5.

$C_8H_{13}O_2Br$ requires Br = 36.2 per cent.

cis(A)-4-Bromo-1-methylcyclohexane-2-carboxylic acid melts at about 103—105°, and dissolves readily in dilute sodium carbonate; when warmed with silver nitrate and nitric acid, it gives an immediate precipitate of silver bromide.

cis(B)-1-Methylcyclohexan-4-ol-2-carboxylic Acid and its Lactone.

The porous plates which had been used in the purification of the acids described in the last section were broken up, extracted with ether in a Soxhlet apparatus, the ethereal solution evaporated, and the residue distilled under 15 mm. pressure, when a considerable quantity of oil passed over at 135—145° and most of the remainder at 185—195° (A).

On refractionating the lower boiling portion, most of it distilled at 126°/15 mm., and this was found on analysis and examination to consist of the lactone of *cis(B)-1-methylcyclohexan-4-ol-2-carboxylic acid* mixed with a large proportion of the lactone of 1-methyl- Δ^6 -cyclohexen-4-ol-2-carboxylic acid (p. 1881).

In order to separate these two lactones, advantage was taken of the fact that the latter acid is slowly converted into the lactone at the ordinary temperature, whereas the former acid is stable under these conditions. The mixed lactones were dissolved in warm dilute potassium hydroxide, cooled well, acidified, and left for seven days, during which time the oily precipitate gradually became less viscid and ultimately comparatively mobile. The whole was several times extracted with ether, the ethereal solution well washed with sodium carbonate, dried and evaporated, and the residue distilled, when almost the entire quantity passed over at 128°/10 mm., and soon crystallised. After draining on porous porcelain and crystallising from light petroleum mixed with a little benzene, the substance melted at 44° and gave the following analytical results :

0.1780 gave 0.4510 CO_2 and 0.1200 H_2O . C = 69.1; H = 7.5.

$C_8H_{10}O_2$ requires C = 69.5; H = 7.2 per cent.

This substance is the lactone of *1-methyl- Δ^6 -cyclohexen-4-ol-2-carboxylic acid*, and identical with the lactone the properties of which are described in detail on p. 1881. The sodium carbonate extract was acidified, and extracted at least five times with ether, when a colourless syrup was obtained which soon solidified. In contact with porous porcelain, the trace of oily impurity was soon removed, and the colourless residue was then crystallised from water, in which it is very readily soluble and from which it separates in glistening crystals :

0.1065 gave 0.2370 CO_2 and 0.088 H_2O . $\text{C} = 60.7$; $\text{H} = 9.0$.

$\text{C}_8\text{H}_{14}\text{O}_3$ requires $\text{C} = 60.8$; $\text{H} = 8.8$ per cent.

0.2150 required for neutralisation 0.0546 NaOH , whereas this amount of a monobasic acid, $\text{C}_8\text{H}_{14}\text{O}_3$, should neutralise 0.0544 NaOH .

cis(B)-1-Methylcyclohexan-4-ol-2-carboxylic acid melts at about 126 — 128° without decomposition, but at 155° decomposition sets in with elimination of steam and formation of the lactone, and at 160 — 162° the disengagement of gas is very rapid. In order to prepare the lactone, the pure acid was distilled under a pressure of 20 mm., when a quantity of oil passed over at 130 — 135° , and, on again distilling, almost the whole quantity passed over at $130^\circ/20$ mm. :

0.1772 gave 0.4475 CO_2 and 0.1356 H_2O . $\text{C} = 68.8$; $\text{H} = 8.5$.

$\text{C}_8\text{H}_{12}\text{O}_2$ requires $\text{C} = 68.6$; $\text{H} = 8.6$ per cent.

This lactone is a rather mobile liquid possessing a faint odour of coumarin ; it is insoluble in cold dilute sodium carbonate or potassium hydroxide, but dissolves readily in the latter on warming, with formation of the salt of the hydroxy-acid.

The oil A (p. 1879), distilling at 185 — $195^\circ/15$ mm., and obtained in considerable quantity during the preparation of the mixed lactones, was refractionated, and, as it distilled remarkably constantly at 184 — $185^\circ/13$ mm., it was thought that it was possibly a pure substance.

The analysis gave the following results :

0.1991 gave 0.4960 CO_2 and 0.1419 H_2O . $\text{C} = 67.9$; $\text{H} = 8.0$,

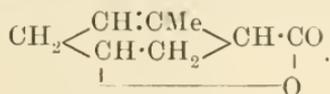
and, as this agrees approximately with the formula $(\text{C}_8\text{H}_{12}\text{O}_2)_2$, which requires $\text{C} = 68.6$; $\text{H} = 8.6$ per cent., it seems probable that the substance is a double lactone of this formula. When this oil was dissolved in dilute potassium hydroxide, the solution acidified, extracted with ether, and the ethereal solution, after thoroughly drying, evaporated to a small bulk, a crystalline acid gradually separated in quantity. This was collected and repeatedly recrystallised from ether, in which it is very sparingly soluble, and from which it separated in crusts melting at 163 — 165° :

0.1254 gave 0.2788 CO₂ and 0.1017 H₂O. C = 60.6; H = 9.0.

C₈H₁₄O₃ requires C = 60.8; H = 8.8 per cent.

Examination showed that this acid is trans(A)-1-methylcyclohexan-4-ol-3-carboxylic acid (compare p. 1877), and it appears therefore that this acid may be distilled under diminished pressure without undergoing intramolecular change into one of the *cis*-modifications.

The Lactone of 1-Methyl-Δ⁶-cyclohexen-4-ol-2-carboxylic Acid,



This lactone was first obtained from the crude product of the reduction of 4-hydroxy-*o*-toluic acid by distillation in a current of steam as explained on p. 1876. The steam distillate (A) was extracted with ether, the ethereal solution dried and evaporated, and the residual viscid syrup left exposed to the air, when it gradually solidified.

Subsequently, a considerable quantity of the same lactone was obtained, mixed with the lactone of *cis*(B)-1-methylcyclohexan-4-ol-2-carboxylic acid, by the process explained on p. 1879.

The crystals were drained on porous porcelain, and crystallised from a mixture of light petroleum and a little benzene, from which the lactone separates in magnificent, glistening prisms, often more than an inch in length:

0.1775 gave 0.4513 CO₂ and 0.1189 H₂O. C = 69.3; H = 7.5.

0.1953 ,, 0.4961 CO₂ ,, 0.1291 H₂O. C = 69.2; H = 7.5.

C₈H₁₀O₂ requires C = 69.5; H = 7.2 per cent.

The lactone of 1-methyl-Δ⁶-cyclohexen-4-ol-2-carboxylic acid melts at 44°, and distils at 128°/10 mm. and at 178—180°/100 mm.

It is readily soluble in benzene, methyl and ethyl alcohols, acetone, and most of the usual organic solvents, with the exception of light petroleum, in which it is rather sparingly soluble.

It is insoluble in cold dilute sodium carbonate, but dissolves gradually on warming, and the solution gives no precipitate on acidifying, but, when boiled, an oil separates, which is doubtless the lactone. It dissolves readily in warm dilute sodium hydroxide, and a quantitative determination of the basicity of the acid produced gave the following result: 1.1264 of the lactone, dissolved in a little methyl alcohol, neutralised 0.356 NaOH on boiling, whereas this amount of a lactone, C₈H₁₀O₂, should neutralise 0.352 NaOH on conversion into the hydroxy-acid. In order, if possible, to obtain the hydroxy-acid, the lactone was dissolved in excess of dilute potassium hydroxide, acidified, and extracted with pure ether, when a very viscid syrup was obtained,

which, after remaining a short time over sulphuric acid, yielded numbers agreeing as closely as could be expected with those required for the hydroxy-acid :

0.2002 gave 0.4545 CO_2 and 0.135 H_2O . C = 61.9 ; H = 7.5.

$\text{C}_8\text{H}_{12}\text{O}_3$ requires C = 61.5 ; H = 7.7 per cent.

When this hydroxy-acid is kept over sulphuric acid, or simply left exposed to the air, it gradually becomes less viscid, and ultimately comparatively mobile, and, after about a week, the oil is almost completely insoluble in cold dilute sodium carbonate, a change which indicates that the hydroxy-acid has been converted into the lactone. The unsaturated nature of the hydroxy-acid is shown by the fact that its solution in dilute sodium carbonate instantly decolorises permanganate, but, in spite of several attempts, a crystalline product of this oxidation could not be isolated.

1 : 4-Dibromo-1-methylcyclohexane-2-carboxylic Acid (Formula, p. 1875).

When the lactone of 1-methyl- Δ^6 -cyclohexen-4-ol-2-carboxylic acid (5 grams) is just melted and mixed with fuming hydrobromic acid (saturated at 0° , 15 c.c.) it dissolves, and, if the solution is left in the ice-chest, crystals gradually begin to separate.

After six days a considerable crust had formed, which was collected, left in contact with porous porcelain over solid potassium hydroxide until quite dry, and the nearly colourless residue crystallised from a mixture of benzene and light petroleum, from which it separated in colourless crusts :

0.2715 gave 0.3335 AgBr. Br = 52.3.

0.2173 ,, 0.2691 AgBr. Br = 53.0 per cent.

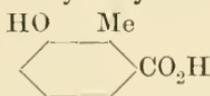
This dibromo-acid softens at 148° and melts at about 158 — 160° with evolution of gas. It is readily soluble in methyl alcohol, ether, benzene, or chloroform, but sparingly so in cold light petroleum. The finely-powdered dibromo-acid dissolves in cold dilute sodium carbonate, but decomposition immediately sets in, with the gradual separation of a heavy oil which has the odour of a bromo-hydrocarbon, and this decomposition is much hastened by warming. Heating with pyridine or diethylaniline appears to produce a similar change.

The authors wish to state that much of the heavy expense of this investigation was defrayed by a grant from the Government Grant Fund of the Royal Society.

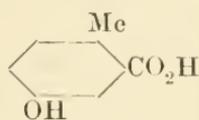
CCVIII.—*The Reduction of 6-Hydroxy-o-toluic Acid.*

By OSCAR BAUDISCH AND WILLIAM HENRY PERKIN, jun.

OSCAR JACOBSEN describes two methods for the preparation of 6-hydroxy-*o*-toluic acid ("β-orthohomometaoxybenzoic acid"), namely, from 6-sulpho-*o*-toluic acid by fusion with potassium hydroxide (*Ber.*, 1883, 16, 1963) and from 6-amino-*o*-toluic acid ("β-amino-*o*-toluic acid") by treatment with nitrous acid (*Ber.*, 1884, 17, 163), and states that it crystallises from water in long, glistening needles of melting point 183°. We have carefully repeated these experiments, and find that the acid of melting point 183° is not 6-hydroxy-*o*-toluic acid (I) as Jacobsen supposed, but 4-hydroxy-*o*-toluic acid (II),



(I.)



(II.)

that is to say, it is identical with the acid of this constitution described in the preceding paper (p. 1875).

There can, therefore, be little doubt that the sulpho-*o*-toluic acid and the amino-*o*-toluic acid employed by Jacobsen in the preparation of this acid of melting point 183° are in both cases the 4- and not the 6-derivatives of *o*-toluic acid.

6-Hydroxy-*o*-toluic acid appears to have been first prepared by Kalle & Co. (D.R.-P. 91201; Friedländer, *Fortschritte der Teerfarbenfabrikation*, IV, 148) from naphthalene-1 : 3 : 5-trisulphonic acid, 2-naphthylamine-4 : 8-disulphonic acid, 1-naphthylamine-3 : 5-disulphonic acid, or 5-amino-1-naphthol-3-sulphonic acid by heating with sodium hydroxide at 250°.

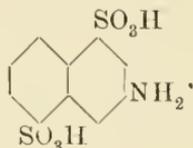
All these derivatives of naphthalene contain the substituting groups in the positions marked by asterisks in the formula



and the decomposition of the molecule by the fused alkali leads to the disruption of the right-hand ring in all cases. Thus, in the case of naphthalene-1 : 3 : 5-trisulphonic acid, the change may be represented in the following manner :



Kalle & Co. state that 6-hydroxy-*o*-toluic acid melts at 141·5—142°, but according to Einhorn and Pfyl (*Annalen*, 1900, 311, 52) this acid melts at 145—146°. The large quantities of 6-hydroxy-*o*-toluic acid which were employed in the present investigation were prepared by heating the sodium salt of 2-naphthylamine-4 : 8-disulphonic acid,

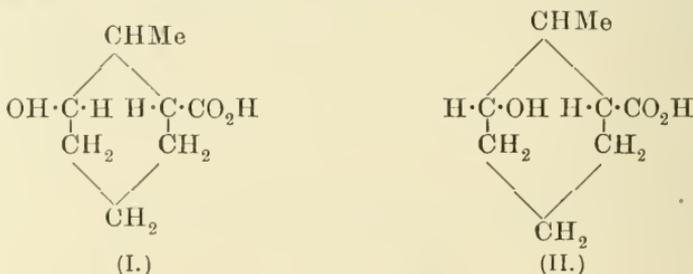


with sodium hydroxide, and we can confirm the statement of Kalle & Co. that the pure acid melts at 141·5—142°.

When 6-hydroxy-*o*-toluic acid is reduced by sodium and alcohol, it yields a mixture of hydroxyhexahydro-acids, from which we have isolated one *trans*- and one *cis*-modification, and, although there was evidence of the presence of a third acid (compare p. 1886), we were unsuccessful in our attempts to obtain it in a pure condition.

trans-1-Methylcyclohexan-2-ol-6-carboxylic acid (I) melts at 170—172°, and, when rapidly heated under diminished pressure, distils for the most part unchanged at about 180°/15 mm. It is converted by treatment with hydrobromic acid into the corresponding syrupy *bromo*-acid.

cis-1-Methylcyclohexan-2-ol-6-carboxylic acid (II) melts at 150°,



and, when heated, is converted into the syrupy lactone, which distils at 128—130°/15 mm., and both the acid and the lactone react with hydrobromic acid with formation of the syrupy *cis*-*bromo*-acid.

The investigation of the unsaturated esters produced by the action of diethylaniline on the esters of the *trans*- and *cis*-*bromo*-1-methylcyclohexane-2-carboxylic acids will form the subject of a future communication.

The Reduction of 6-Hydroxy-o-toluic Acid.

The 6-hydroxy-*o*-toluic acid required for these experiments was obtained by heating sodium 2-naphthylamine-4:8-disulphonate* (1 kilo.) with sodium hydroxide (4 kilos. of 50 per cent.) in an autoclave for ten hours at 250—260°, when decomposition took place slowly with the development of great pressure, due principally to the formation of large quantities of ammonia. The product was mixed with a little water, nearly neutralised with hydrochloric acid, filtered, and then acidified with excess of hydrochloric acid. After remaining overnight, the precipitate was collected, washed with water, and crystallised from water with the aid of animal charcoal.

The acid obtained in this way melts at 141·5—142°, and is pure 6-hydroxy-*o*-toluic acid, but the yield obtained is unfortunately not more than 10 per cent. of that theoretically possible, so that the preparation of the large quantities of this acid which were required for this investigation was very laborious, and, indeed, necessitated the fusion of 14 kilos. of the sodium salt of 2-naphthylaminedisulphonic acid with sodium hydroxide. A small quantity of the pure hydroxy-acid was converted, by treatment with alcohol and sulphuric acid in the usual manner, into ethyl 6-hydroxy-*o*-toluate, which melted at 69°, as stated by Kalle & Co. (*loc. cit.*), and yielded on analysis:

0·1614 gave 0·3935 CO₂ and 0·0980 H₂O. C = 66·5; H = 6·7.

C₁₀H₁₂O₃ requires C = 66·7; H = 6·7 per cent.

The reduction of 6-hydroxy-*o*-toluic acid by means of sodium and alcohol was carried out under the conditions described in detail in the case of the reduction of 4-hydroxy-*o*-toluic acid (p. 1876) and in the same apparatus. The product of the reduction, after the removal of the alcohol, was acidified with excess of hydrochloric acid, extracted four times with ether, the ethereal solution carefully dried, evaporated, the residual syrupy mixture of hydroxy-acids† esterified, and the esters fractionated under diminished pressure, when a large quantity of a pale yellow, viscid oil passed over at 140—180°/15 mm., leaving a considerable amount of a brown resin in the distilling flask. On refractionating, a small quantity of an unsaturated ester passed over below 130°/15 mm., and then the mixed hydroxy-esters distilled at about 145—147°/15 mm. This ester (60 grams) was mixed with potassium

* We are greatly indebted to Messrs. Cassella & Co. for a large supply of this valuable salt.

† It is stated on p. 1876 that the crude product of the reduction of 4-hydroxy-*o*-toluic acid yields an unsaturated lactone in considerable quantity when it is distilled in a current of steam, but only traces of an unsaturated lactone were obtained when the crude product of the reduction of the 6-hydroxy-acid was similarly treated.

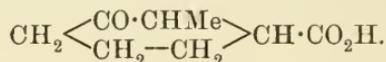
hydroxide (30 grams) in methyl alcohol, and, after remaining overnight, the product was heated for one hour on the water-bath, water was then added, the alkaline solution saturated with carbon dioxide, evaporated until free from methyl alcohol, acidified, and extracted eight times with ether. After drying over anhydrous sodium sulphate, the ethereal solution was evaporated, and the amber syrup left for several days exposed to the air and until crystallisation appeared to be complete, a process which was much hastened by stirring from time to time. The mass was left in contact with porous porcelain until free from oily impurity, and the colourless residue systematically crystallised from dry ether and then from water, when it gradually separated into *trans*-1-methylcyclohexan-2-ol-6-carboxylic acid, melting at 170—172°, and the corresponding *cis*-acid, melting at 150—151°, the former being the less soluble, but there was also present a considerable quantity of a more soluble acid, which melted at about 128—133°, and gave the following results on analysis:

0·1704 gave 0·3795 CO₂ and 0·1396 H₂O. C = 60·7; H = 9·2.

C₈H₁₄O₃ requires C = 60·8; H = 8·8 per cent.

This acid appears to be a second *cis*-modification, but we were unable, in spite of many crystallisations from different solvents, to obtain it quite free from the other modifications.

1-Methylcyclohexan-2-one-6-carboxylic Acid,



A quantity of the acid just described, melting at 128—133° (15 grams), dissolved in water (200 c.c.) was gradually oxidised on the water-bath with potassium dichromate (11 grams) dissolved in water (100 c.c.) and sulphuric acid (15 grams). The product was saturated with ammonium sulphate, extracted, the viscid syrup mixed with excess of semicarbazide hydrochloride and sodium acetate, and the semicarbazone, which gradually separated, collected, washed well, decomposed with dilute hydrochloric acid, and the keto-acid extracted with ether.

The syrup, obtained on distilling off the ether, crystallised, and, after washing with small quantities of dry ether on porous porcelain, the colourless residue gave numbers agreeing approximately with those required for *1-methylcyclohexan-2-one-6-carboxylic acid*:

0·1425 gave 0·3172 CO₂ and 0·1081 H₂O. C = 60·7; H = 8·4.

C₈H₁₂O₃ requires C = 61·5; H = 7·7 per cent.

This acid melted at about 97°, but, since it was not found possible

to recrystallise it satisfactorily, this melting point can only be approximate. The keto-acid is very soluble in water, and its behaviour seemed to indicate that it was a mixture of *cis*- and *trans*-isomerides. The solution of the acid gives no immediate precipitate with semicarbazide hydrochloride and sodium acetate, but the *semicarbazone* soon begins to separate in flakes, and melts at about 200—205° with decomposition:

0·1320 gave 22 c.c. N₂ at 18° and 762 mm. N = 19·5.

C₉H₁₅O₃N₃ requires N = 19·7 per cent.

trans-1-Methylcyclohexan-2-ol-6-carboxylic Acid.

This acid melts at about 170—172°, is sparingly soluble in cold ether, and separates, when the solution is concentrated and rapidly cooled, in colourless, crystalline crusts. If, however, the solution is allowed to cool very slowly or to evaporate spontaneously, the acid separates in well defined, glistening prisms, like sugar crystals. It is readily soluble in water, and separates from this solvent in characteristic woolly balls. Two different specimens crystallised from ether and water respectively gave the following results on analysis:

0·1420 gave 0·3160 CO₂ and 0·1160 H₂O. C = 60·7; H = 9·0.

0·1706 „ 0·3788 CO₂ „ 0·1397 H₂O. C = 60·5; H = 9·1.

C₈H₁₄O₃ requires C = 60·8; H = 8·8 per cent.

On titration with *N*/10-sodium hydroxide, 0·3011 neutralised 0·0761 NaOH, whereas this amount of a monobasic acid, C₈H₁₄O₃, should neutralise 0·0762 NaOH. The *trans*-hydroxy-acid dissolves readily in hydrobromic acid (saturated at 0°), and there is no apparent change at the ordinary temperature even after several days, but, when heated on the water-bath, the solution clouds, and a syrup separates which analysis showed to consist of almost pure *trans*-6-bromo-1-methylcyclohexane-2-carboxylic acid. Several attempts were made to obtain the corresponding keto-acid by oxidising the *trans*-hydroxy-acid with dichromate, but without success. When the theoretical amount of oxidising agent was employed, a good deal of unchanged hydroxy-acid was always recovered, and excess of oxidising agent apparently caused profound decomposition, since only a trace of a keto-acid could be isolated, and that in an impure state.

cis-1-Methylcyclohexan-2-ol-6-carboxylic Acid and its Lactone.

The porous plates which had been used in the purification of the *cis*- and *trans*-acids (p. 1886) were broken up, extracted with ether in a Soxhlet apparatus, the extract mixed with the residue obtained when the various mother liquors from the purification of the *cis*- and *trans*-

acids was evaporated, and the whole (80 grams) distilled under 15 mm. pressure. A considerable quantity passed over below 155° and most of the remainder distilled at 180—195°, and when the oil of lower boiling point was redistilled, a considerable quantity of a rather mobile oil was obtained, which distilled constantly at 128—130°/15 mm. :

0·1670 gave 0·4180 CO₂ and 0·1330 H₂O. C = 68·2 ; H = 8·8.

0·1665 ,, 0·4192 CO₂ ,, 0·1310 H₂O. C = 68·6 ; H = 8·7.

C₈H₁₂O₂ requires C = 68·6 ; H = 8·6.

This substance is the *lactone* of *cis*-1-methylcyclohexan-2-ol-6-carboxylic acid, and is a colourless oil possessing the peculiar odour characteristic of cyclic lactones. It is insoluble in sodium carbonate and cold dilute potassium hydroxide, but dissolves readily in the latter on warming, with formation of the salt of the *cis*-hydroxy-acid. In order to obtain the free acid, the well cooled alkaline solution was acidified, extracted several times with ether, the ethereal solution dried, and evaporated at a low temperature, when a colourless syrup was obtained which rapidly crystallised.

After remaining in contact with porous porcelain until quite dry, the colourless residue separated from ether in glistening crusts, melted at 149—150°, and was identical with the *cis*-acid obtained directly from the product of the reduction of 6-hydroxy-*o*-toluic acid (p. 1886). Of the following analyses, the first was made with material obtained directly from the reduction, and the second with a specimen of the acid which had been prepared from the lactone :

0·1565 gave 0·3476 CO₂ and 0·1289 H₂O. C = 60·6 ; H = 9·2.

0·2088 ,, 0·4645 CO₂ ,, 0·1720 H₂O. C = 60·7 ; H = 9·1.

C₈H₁₄O₃ requires C = 60·8 ; H = 8·8 per cent.

0·3117 neutralised 0·0784 NaOH, whereas the theory for this quantity of a monobasic acid, C₈H₁₄O₃, is 0·0788 NaOH.

cis-1-Methylcyclohexan-2-ol-6-carboxylic acid melts at 150—151°, and decomposes slowly at 165°, but much more rapidly at 180° into steam and the lactone. It is readily soluble in water, but sparingly so in cold dry ether. The powdered acid dissolves readily in fuming hydrobromic acid (saturated at 0°), but, even after several days, no separation of the bromo-acid takes place at the ordinary temperature. When, however, the solution is heated on the water-bath, the *cis*-bromo-acid separates as a viscid layer on the surface of the hydrobromic acid. The lactone of the *cis*-hydroxy-acid dissolves at once in fuming hydrobromic acid with slight evolution of heat, and, when left overnight, the liquid clouds and a viscid syrup separates, a change which takes place rapidly on warming.

The product was diluted with water, extracted with ether, the

etheral solution well washed, dried, evaporated, and the residue left for a short time over sulphuric acid in an evacuated desiccator.

Analysis then yielded the following numbers, which agree well with those required for *cis*-6-bromo-1-methylcyclohexane-2-carboxylic acid:

0.1798 gave 0.1528 AgBr. Br = 36.1.

$C_8H_{13}O_2Br$ requires Br = 36.2 per cent.

The viscid oil, described at the beginning of this section, which distilled at 180—195°/15 mm., was again fractionated, when it distilled remarkably constantly at 185°/15 mm., and gave, on analysis, C = 63.6 and H = 8.5 per cent. When this syrup was stirred well with dry ether (2 vols.) and left for several days, a crust separated, which, after crystallising from ether, melted at 169—170°, and gave on analysis the following result:

0.1173 gave 0.2065 CO_2 and 0.0971 H_2O . C = 60.7; H = 9.2.

$C_8H_{14}O_3$ requires C = 60.8; H = 8.9 per cent.

That this acid was *trans*-1-methylcyclohexan-2-ol-6-carboxylic acid was proved by mixing it with a specimen of this acid which had been obtained by the method described on p. 1886, when the mixture melted at 168—170°. The above experiment clearly demonstrates that the acid of melting point 169—170° distils without the formation of a lactone, and confirms the view adopted in this communication that it is *trans*-1-methylcyclohexan-2-ol-6-carboxylic acid.

THE UNIVERSITY,
MANCHESTER.

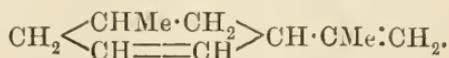
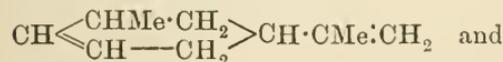
CCIX.—*The Reduction of 5-Hydroxy-m-toluic Acid.*

By ANDREW NORMAN MELDRUM (Carnegie Research Fellow) and
WILLIAM HENRY PERKIN, jun.

THE present investigation was undertaken with the object of preparing unsaturated acids of the constitution

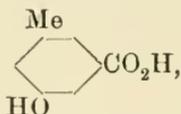


in order, with their aid, to attempt the synthesis of the two terpenes:

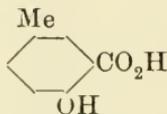


These terpenes are of considerable interest, not only because they are unknown members of the meta-series, but also because it is possible that one of them may be the inactive modification of sylvestrene, the constitution of which is still doubtful.

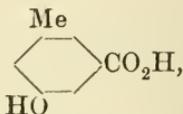
In order to synthesise the unsaturated acids figured above, it was necessary to prepare large quantities of 5-hydroxy-*m*-toluic acid,



and this proved to be a task of considerable difficulty. This acid appears to have been first prepared by Jacobsen (*Ber.*, 1881, 14, 2357) from *m*-toluic acid by sulphonation and subsequent fusion with potassium hydroxide. Jacobsen showed that *m*-toluic acid is converted by treatment with fuming sulphuric acid at 160° into a mixture of sulphonic acids which, on fusion, yields, besides small quantities of isophthalic acid and α -hydroxyisophthalic acid, the following hydroxy-*m*-toluic acids :



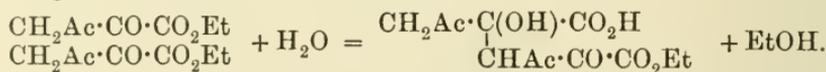
4-Hydroxy-*m*-toluic Acid. M. p. 149°.



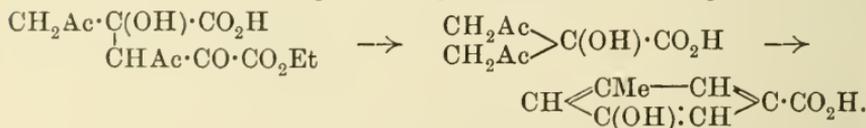
5-Hydroxy-*m*-toluic Acid. M. p. 208°.

and these, he states, are produced in approximately equal quantities.

At a later date, Claisen and Stylos (*Ber.*, 1887, 20, 2188 ; compare Claisen, *Ber.*, 1889, 22, 3271, and Tingle, "Ueber die Einwirkung von Oxaläther auf aliphatische Ketone," *Inaug. Diss.*, Munich, 1889) showed that 5-hydroxy-*m*-toluic acid may be synthesised from ethyl acetoneoxalate by the following interesting series of reactions. The sodium derivative of ethyl acetoneoxalate is decomposed by water and dilute acids with formation of an acid, C₁₂H₁₆O₈ (m. p. 91°), a decomposition which Claisen formulates thus :

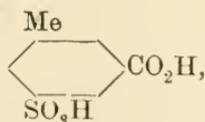


When this acid is digested with barium hydroxide, it is decomposed with elimination of oxalic acid and formation of 5-hydroxytoluic acid, diacetoneoxalic acid being evidently an intermediate stage :

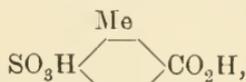
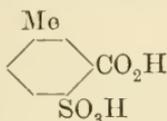


It seemed at first likely that this elegant synthesis might prove to be the most convenient method for obtaining the 5-hydroxy-*m*-toluic acid required for this research, but careful investigation, under a

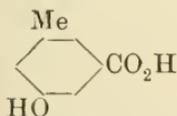
variety of conditions, showed that, whilst it is an excellent method for the rapid preparation of small quantities, it is unsuitable, principally owing to the large volumes of liquid involved, for the preparation of large quantities. We therefore returned to Jacobsen's method and investigated, in considerable detail, the sulphonation of *m*-toluic acid. We found that *m*-toluic acid is readily sulphonated at 160° by pure sulphuric acid and, under these conditions, the principal product is 5-sulpho-*m*-toluic acid,



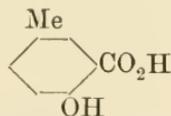
but considerable quantities of the 4- and 6-sulphonic acids,



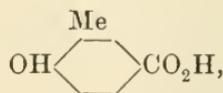
are always produced at the same time. When these sulphonic acids are fused with potassium hydroxide, they yield the three hydroxy-*m*-toluic acids,



5-Hydroxy-*m*-toluic Acid. M. p. 208°



4-Hydroxy-*m*-toluic Acid. M. p. 150°.



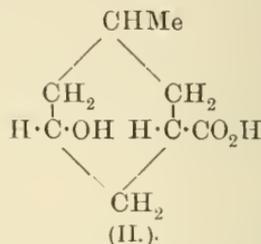
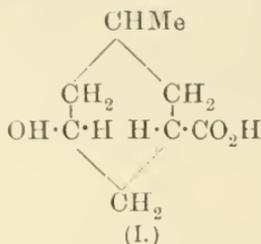
6-Hydroxy-*m*-toluic Acid. M. p. 172°.

and as the yield of the 5-hydroxy-acid is satisfactory, this method was adopted for the preparation of almost the whole of the acid required for the present investigation. 5-Hydroxy-*m*-toluic acid is not so readily reduced by sodium and alcohol as *m*-hydroxybenzoic acid (Trans., 1907, 91, 486), but reduction takes place quickly and almost completely in boiling *iso*amyl-alcoholic solution.

It is rather remarkable, in view of our experience in other similar cases (compare Trans., 1908, 93, 1417, and the two preceding communications), that, although four stereoisomeric 1-methylcyclohexan-3-ol-5-carboxylic acids might result from this reduction, we have only been able to isolate one acid of melting point 138—139°, and, if any of the other possible acids are produced at all, it must be in very small quantities. The careful investigation of its properties has shown that the acid of melting point 138—139° is *trans*-1-methylcyclohexan-3-ol-5-carboxylic acid (I).

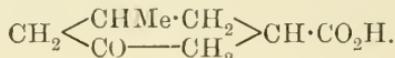
When the crude *trans*-acid is distilled, it is converted partly into the lactone of the *cis*-acid (b. p. 130—132°/13 mm.), and this, on hydrolysis,

yields pure *cis*-1-methylcyclohexan-3-ol-5-carboxylic acid (II), which, like the *trans*-modification, melts at 138—139°, but the careful investigation of their properties clearly proves that the two acids are



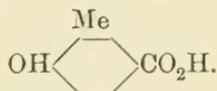
distinct. Both the *cis*- and *trans*-hydroxy-acids are converted by fuming hydrobromic acid into the corresponding *bromo*-acids, and these, on treatment with diethylaniline, yield unsaturated acids, the investigation of which is in progress.

When ethyl *trans*-1-methylcyclohexan-3-ol-5-carboxylate is oxidised with chromic acid, it is converted into *ethyl*-1-methylcyclohexan-3-one-5-carboxylate, which distills at 138—140°/15 mm., and, on hydrolysis, yields the corresponding acid,

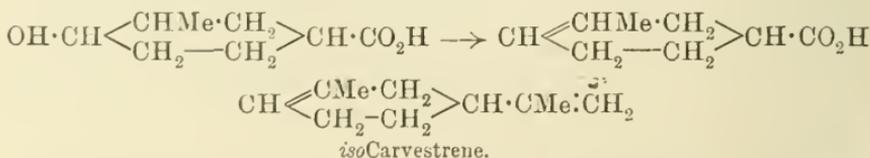


This syrupy keto-acid distills at 192°/15 mm., and yields a crystalline oxime (m. p. 142°), but does not appear to combine readily with semicarbazide.

It has already been stated that one of the acids resulting from the sulphonation of *m*-toluic acid is 6-sulpho-*m*-toluic acid, and that this, on fusion with potassium hydroxide, yields 6-hydroxy-*m*-toluic acid,



This acid is of special interest in connexion with the experiments on the synthesis of the terpenes, because if it could be reduced by sodium and alcohol, it would yield 1-methylcyclohexan-2-ol-5-carboxylic acid, from which, by elimination of water and subsequent treatment with magnesium methyl iodide, *isocarvestrene* should result :



The actual process employed in the synthesis of *isocarvestrene* and its derivatives (Fisher and Perkin, *Trans.*, 1908, **93**, 1877) is a complicated and very laborious one, and, as the method indicated above would be much more direct and considerable quantities of 6-hydroxy-

m-toluic acid had accumulated, a series of experiments was made with the object of reducing it to the corresponding hexahydroderivative.

The acid was treated with ethyl alcohol and sodium and with *iso*-amyl alcohol and sodium under a variety of conditions, but in no case could any indication of reduction be observed, a result in harmony with a series of unsuccessful experiments which had previously been made in the hope of reducing *p*-hydroxybenzoic acid under similar circumstances.

Sulphonation of m-Toluic Acid.

After a series of comparative experiments, the following process was adopted for the sulphonation of the large quantities of *m*-toluic acid which were required for this investigation. The pure acid (250 grams) and pure sulphuric acid (750 c.c.) are heated in a bolt-head at 180° for eight hours, the temperature being carefully regulated by a gas regulator, and the whole being stirred or agitated from time to time in order to ensure perfect mixture. The product is allowed to cool, mixed with water (900 c.c.), and left overnight, when a mass of small crystals gradually forms, and when the separation is complete, the whole is filtered through flannel by the aid of the pump and drained on porous porcelain. The filtrate (A) was kept for further examination (p. 1894). The crude 5-sulpho-*m*-toluic acid thus obtained is crystallised either from water or by adding hydrochloric acid to the concentrated aqueous solution,* and a specimen which had been repeatedly recrystallised melted at 110° and gave the following results on analysis :

0.2506 neutralised 0.0794 NaOH, whereas this amount of a dibasic acid, $C_8H_8O_5S_2 \cdot 2H_2O$, should neutralise 0.0795 NaOH, and this result was confirmed by the titration of several different specimens.

5-Sulpho-*m*-toluic acid yields two very characteristic salts.

The Sodium Hydrogen Salt, $C_8H_7O_5SNa \cdot 2H_2O$.—This beautifully crystalline salt separates when hydrochloric acid is added to the concentrated solution of the neutral sodium salt, and is readily purified by crystallisation from water, from which it separates in glistening plates :

0.2401 gave 0.0614 Na_2SO_4 . Na = 8.29.

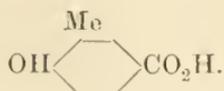
0.2813, heated at 140° until constant, lost 0.0372. $H_2O = 13.22$.

$C_8H_7O_5SNa \cdot 2H_2O$ requires Na = 8.4 ; $H_2O = 13.14$ per cent.

The titration of this salt with *N*/10-sodium hydroxide gave the following results :

* The mother liquors (B) from these crystallisations were carefully investigated (p. 1895).

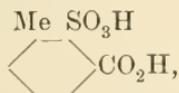
tion with ferric chloride, and proved to be 6-hydroxy-*m*-toluic acid,



Evidently, then, one of the products of the sulphonation of *m*-toluic acid is 6-sulpho-*m*-toluic acid.

The mother-liquors (B, p. 1893) from the crystallisation of the crude sulphonic acid, and which had accumulated in considerable quantity, were freed from sulphuric acid by treatment with the exact quantity of barium hydroxide in the usual manner. The filtrate from the barium sulphate was divided into halves, one of which was neutralised with barium carbonate, the other was then added and the liquid concentrated. The first crop which separated consisted of the hydrogen barium salt of 5-sulpho-*m*-toluic acid, since, after conversion into the potassium salt and fusion with potassium hydroxide, it yielded 5-hydroxy-*m*-toluic acid (m. p. 208°).

The more soluble salt consisted essentially of the hydrogen barium salt of 6-sulpho-*m*-toluic acid, and yielded, after conversion into the potassium salt and fusion with potassium hydroxide, 6-hydroxy-*m*-toluic acid (m. p. 173°). During this series of experiments, although careful search was made, there was no indication of the presence of 2-sulpho-*m*-toluic acid,



and it seems probable that this isomeride is not formed during the sulphonation of *m*-toluic acid.

5-Hydroxy-m-toluic Acid

This acid was prepared in large quantities (about 1500 grams) for the purposes of this research, and every effort was made to obtain it in as pure a condition as possible. The sulphonic acid employed was twice recrystallised from water, and then added, in quantities of 50 grams, to potassium hydroxide (150 grams), and the whole gradually heated (during about half an hour), with constant stirring, until the temperature reached 260°.

The product was dissolved in water, nearly neutralised with hydrochloric acid, mixed with a little animal charcoal, concentrated, and, after remaining overnight, the filtrate from the animal charcoal and potassium chloride was acidified and the crystalline acid collected and well washed. In order to purify the acid further, it was converted

into the characteristic calcium salt, $(C_8H_7O_3)_2Ca, 2H_2O$, described by Jacobsen (*Ber.*, 1881, 14, 2358), and for this purpose the acid was ground to a paste with water, digested with precipitated calcium carbonate, and the filtrate concentrated, when the salt separated in magnificent, glistening prisms. This salt was recrystallised until quite pure, and a specimen yielded, on analysis, numbers confirming the composition assigned to it by Jacobsen.

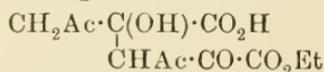
0.3058, heated at 100° until constant, lost $0.0296 H_2O$, and gave on ignition $0.0448 CaO$. $H_2O = 9.68$; $Ca = 10.47$.

$C_{16}H_{14}O_6Ca, 2H_2O$ requires $H_2O = 9.52$; $Ca = 10.58$ per cent.

Finally, the pure salt was dissolved in boiling water, acidified with hydrochloric acid, the acid collected, and crystallised once from water ; it then melted at 208° , and consisted of pure 5-hydroxy-*m*-toluic acid. The yield obtained from *m*-toluic acid varied considerably in different preparations, but was usually about 40 per cent.

During the earlier stages of this research, we attempted to prepare the 5-hydroxy-*m*-toluic acid required from ethyl oxalate and acetone by the method described by Claisen and Miller (*Ber.*, 1899, 22, 3271), but, at first, without success. Subsequently, Dr. J. B. Tingle was kind enough to send us a copy of his dissertation which deals with this series of reactions, but does not appear to have been published, and, by modifying the process in some of its details, we ultimately prepared considerable quantities of 5-hydroxy-*m*-toluic acid in this way, but the method was found to be more laborious than that based on the sulphonation of *m*-toluic acid.

Sodium (23 grams) was dissolved in absolute alcohol (350 c.c.), and the solution added to a mixture of acetone (58 grams) and ethyl oxalate (146 grams), when, after some time, the whole became semi-solid, owing to the separation of the sodium derivative of ethyl acetoneoxalate, $CHAcNa \cdot CO \cdot CO_2Et$. This was collected, transferred to a bottle, and shaken mechanically with glacial acetic acid (300 c.c.) for two hours. The crystalline precipitate which had separated, and contained about 6.7 per cent. of sodium, was collected, washed with ether, ground up with water and excess of dilute sulphuric acid, and the colourless, crystalline precipitate melting at 89° , and consisting of the substance



(see p. 1890), collected and digested in quantities of 100 grams with a solution of barium hydroxide (155 grams) in water (1 litre) on the water-bath. After about thirty minutes, the barium oxalate was removed by filtration, the filtrate neutralised, concentrated, and acidified, when crude 5-hydroxy-*m*-toluic acid (28 grams) separated, and, after one crystallisation from water, melted at 208° , and was quite pure.

The Reduction of 5-Hydroxy-m-toluic Acid.

Since preliminary experiments showed that this acid is not readily reduced by sodium and alcohol, we decided, in the first place, to investigate its behaviour on reduction with sodium and *isoamyl* alcohol. The pure acid (35 grams) was dissolved in *isoamyl* alcohol (1300 c.c.), the solution heated to boiling, and then sodium (130 grams) added as rapidly as possible. When all the sodium had dissolved, the mass was mixed with water, the *isoamyl* alcohol layer separated, washed several times with water, and the combined aqueous layers neutralised and evaporated to a small bulk.

The sodium chloride which crystallised out was removed, and the filtrate acidified, when a syrup separated which soon began to crystallise. After remaining for several days in the ice-chest, the crystalline mass was collected, and left in contact with porous porcelain until quite free from oil, when the almost colourless residue weighed 17 grams. This was ground with a little ether, washed with ether, and repeatedly crystallised from water :

0.1347 gave 0.2996 CO_2 and 0.1058 H_2O . C = 60.7 ; H = 8.7.

$\text{C}_8\text{H}_{14}\text{O}_3$ requires C = 60.8 ; H = 8.8 per cent.

0.3420, dissolved in water and titrated with *N*/10-sodium hydroxide, required 0.0862 NaOH for neutralisation, whereas the theoretical amount is 0.0865 NaOH.

trans-1-Methylcyclohexan-3-ol-5-carboxylic acid melts at 138—139°, and, unlike the *cis*-acid, shows no signs of decomposing at 150°; when, however, it is heated at 180°, slow decomposition sets in, and becomes rapid at 200°. It is readily soluble in hot water, and separates on cooling in crystalline crusts.

In ether it is very sparingly soluble, and when the warm saturated solution is concentrated, the acid separates after some time in crystalline crusts, which are bright white under the ether, but, when exposed to the air, rapidly become chalky. The salts of the acid do not crystallise well. The ammonium, potassium, and sodium salts are very soluble in water, and the solutions of the calcium and barium salts, when concentrated, set to jellies.

The *trans*-acid dissolves readily in fuming hydrobromic acid (saturated at 0°), and separation of crystals does not occur when the solution is left for forty-eight hours (compare the behaviour of the *cis*-acid under the same conditions). If the solution is allowed to evaporate over potassium hydroxide and sulphuric acid in a vacuum desiccator, a gummy acid containing bromine remains. The clear solution of the *trans*-acid in hydrobromic acid gradually clouded on the water-bath and, in a few minutes, an oily layer separated on the

surface, and when separation was complete, the whole was diluted with water, extracted with ether, the ethereal solution washed, dried, evaporated and left exposed over sulphuric acid in a vacuum desiccator for several hours. The nearly colourless syrup yielded the following results on analysis :

0.2857 gave 0.2346 AgBr. Br = 35.1.

$C_8H_{13}O_2Br$ requires Br = 36.2 per cent.

This substance is evidently nearly pure *trans-5-bromo-1-methylcyclohexane-3-carboxylic acid*.

cis-1-Methylcyclohexan-3-ol-5-carboxylic Acid.

The porous plates used in the purification of the *trans*-acid were extracted with ether in a Soxhlet apparatus, and the crude syrup remaining after the removal of the ether slowly distilled under 12 mm. pressure. At first much water was given off, and then an oil distilled at 120—160°, followed by a considerable quantity of a pale yellow oil distilling at 210—220°. The oil of lower boiling point yielded, on repeated fractionation, a lactone distilling at 130—132°/13 mm. :

0.2081 gave 0.5226 CO_2 and 0.1655 H_2O . C = 68.5 ; H = 8.8.

$C_8H_{12}O_2$ requires C = 68.6 ; H = 8.6 per cent.

This *lactone* of *cis-1-methylcyclohexan-3-ol-5-carboxylic acid* has the odour characteristic of lactones of this nature; it is insoluble in sodium carbonate and dilute potassium hydroxide in the cold, but dissolves readily in the latter on warming. In order to prepare the corresponding hydroxy-acid, the lactone was dissolved in hot dilute potassium hydroxide, the solution cooled, acidified, and extracted several times with pure ether. The ethereal solution was carefully dried and concentrated, when it was noticed that, at a certain concentration, a crystalline acid commenced to separate from the boiling ethereal solution, and the amount increased considerably on standing. After recrystallising twice from ether, the acid was quite pure, and yielded the following results on analysis :

0.1212 gave 0.2700 CO_2 and 0.0959 H_2O . C = 60.7 ; H = 8.8.

$C_8H_{14}O_3$ requires C = 60.8 ; H = 8.8 per cent.

The basicity of the acid was determined by titration with *N*/10-sodium hydroxide, when 0.2221 neutralised 0.0556 NaOH, whereas this amount of a monobasic acid, $C_8H_{14}O_3$, should neutralise 0.0562 NaOH.

cis-1-Methylcyclohexan-3-ol-5-carboxylic acid melts at 138—139° and decomposes slowly at 140°, but much more rapidly at 150°.

It is very readily soluble in water, but sparingly so in ether, and separates from its solution in the latter solvent, on concentrating, as

a soft, crystalline mass consisting of pearly plates, which do not lose their lustre on exposure to air. In this respect it shows a marked difference from the behaviour of the *trans*-acid in the same circumstances. Both the *trans*- and the *cis*-acids melt at the same temperature (139°), but an intimate mixture of equal amounts of the two isomerides shrinks at 115°, and is almost melted at 120°. Again, the two acids exhibit a striking difference in their behaviour towards hydrobromic acid, by the action of which the *trans*-acid, as already explained, is converted into a syrupy bromo-acid. The *cis*-acid dissolves readily in fuming hydrobromic acid (saturated at 0°), and the solution soon begins to deposit crystals. After remaining overnight, the whole was transferred to porous porcelain, and left until the hydrobromic acid had been completely absorbed; the residue was then dried over sulphuric acid and solid potassium hydroxide in a vacuum desiccator.

The colourless bromo-acid was purified by crystallisation from light petroleum (b. p. 50–60°), and two different specimens gave the following results on analysis:

0.2878 gave 0.2499 AgBr. Br = 36.8.

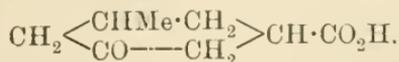
0.2869 „ 0.2448 AgBr. Br = 36.4.

$C_8H_{13}O_2Br$ requires Br = 36.2 per cent.

cis-5-Bromo-1-methylcyclohexane-3-carboxylic acid melts at 90–92°, and decomposes, with effervescence but with little change in colour, at about 170°. It is very readily soluble in alcohol, ether, or benzene, but somewhat less so in light petroleum, from which it separates in brilliant prisms or, if the hot concentrated solution is rapidly cooled, in glistening, needle-shaped leaflets.

It is a comparatively stable substance, and is only gradually decomposed on boiling with water.

1-Methylcyclohexan-3-one-5-carboxylic Acid,



In preparing this acid, chromic acid (5 grams), dissolved in a little water, was gradually added to ethyl 1-methylcyclohexan-3-ol-5-carboxylate (10 grams) dissolved in acetic acid (10 c.c.), care being taken that the temperature did not rise above 40°.

After about three hours, the product was mixed with very dilute sulphuric acid, extracted with ether, the ethereal solution washed well with water and then with sodium carbonate, dried, and evaporated.

The residue yielded, on repeated fractionation, *ethyl* 1-methylcyclo-

hexan-3-one-5-carboxylate as a colourless oil distilling at 138—140°/15 mm. :

0.1411 gave 0.3366 CO₂ and 0.1128 H₂O. C = 64.9 ; H = 8.9.

C₁₀H₁₆O₃ requires C = 65.2 ; H = 8.7 per cent.

In order to obtain the free acid, this ester (15 grams) was digested with dilute hydrochloric acid (150 c.c. of 5 per cent.) in a reflux apparatus, the condenser of which was removed from time to time to allow the alcohol to escape. The clear solution was saturated with ammonium sulphate, when an oil separated which was extracted several times with ether, the ethereal solution was then dried, evaporated, and the colourless syrup distilled :

0.1651 gave 0.3737 CO₂ and 0.1173 H₂O. C = 61.7 ; H = 7.9.

0.1320 „ 0.2980 CO₂ „ 0.0931 H₂O. C = 61.6 ; H = 7.8.

C₈H₁₂O₃ requires C = 61.5 ; H = 7.7 per cent.

1-Methylcyclohexan-3-one-5-carboxylic acid is a viscid syrup, which distils at 192°/15 mm., and a strong solution of which in water clouds on cooling. The titration of the acid with *N*/10-sodium hydroxide yielded the following results :

0.2064 neutralised 0.052 NaOH, whereas this amount of a monobasic acid, C₈H₁₂O₃, should neutralise 0.053 NaOH.

The aqueous solution of the acid did not yield a crystalline semicarbazone on the addition of sodium acetate and semicarbazide hydrochloride even on standing for several hours, but, on the other hand, a crystalline oxime was readily obtained.

In order to prepare this, the acid (2 grams), dissolved in a little water, was mixed with a strong solution of hydroxylamine hydrochloride (4 grams) and potassium hydroxide (6 grams) and left for several hours. The alkaline solution was acidified, repeatedly extracted with ether, the ethereal solution dried and evaporated, when a colourless syrup remained which gradually crystallised.

The mass was left in contact with porous porcelain until quite free from oil, and then recrystallised from ether :

0.1755 gave 11.8 c.c. N₂ at 15° and 764 mm. N = 7.9.

C₈H₁₃O₃N requires N = 8.2 per cent.

3-Oximino-1-methylcyclohexan-5-carboxylic acid is readily soluble in warm, but much less so in cold, ether, and separates from this solvent in minute prisms, melting at 142°.

The authors are indebted to the Carnegie Trust and to the Chemical Society for grants which have largely defrayed the cost of this investigation.

CCX.—*The Formation and Reactions of Imino-compounds. Part XI. The Formation of 1-Imino-2-cyanocyclopentane from Adiponitrile.*

By JOCELYN FIELD THORPE.

It has been already shown that open-chain compounds containing two nitrile groups separated by four carbon atoms tend readily to pass into derivatives of the five-membered ring when they are treated in alcoholic solution with a trace of sodium ethoxide or of a sodium compound which dissociates in alcohol, the two instances illustrating this generalisation being the transformation of ethyl $\alpha\delta$ -dicyanovaleate into ethyl 2-imino-3-cyanocyclopentane-1-carboxylate (this vol., 685),



and the production of β -imino- α -cyanohydrindene from *o*-phenylenediacetonitrile (Trans., 1908, 93, 176),

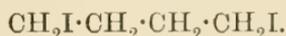


In order, therefore, to show that this reaction is of general application when applied to the formation of the *cyclopentane* ring, it remained to prove that adiponitrile passed with equal readiness into 1-imino-2-cyanocyclopentane,



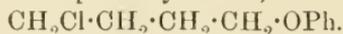
Experiment showed that this reaction took place with great ease, and that it was only necessary to heat an alcoholic solution of the dinitrile containing a trace of sodium ethoxide for a short time on the water-bath in order to transform it completely into the cyclic imino-nitrile.

The adiponitrile used in these experiments was prepared according to the directions of Henry (*Bull. Acad. roy. Belg.*, 1901, 7, 367) by the action of alcoholic potassium cyanide on $\alpha\delta$ -di-iodobutane,



After several methods had been tried for the preparation of this iodo-compound in a pure condition, the process recommended by von Braun (*Ber.*, 1906, 39, 4357) was ultimately found to give the best results. This process starts with $\alpha\gamma$ -dibromopropane, $\text{CH}_2\text{Br} \cdot \text{CH}_2 \cdot \text{CH}_2\text{Br}$, which is converted into α -bromo- γ -phenoxypropane, $\text{CH}_2\text{Br} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OPh}$, by the action of sodium phenoxide. This compound is then converted into γ -phenoxybutyronitrile, $\text{CN} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OPh}$, by the action of

potassium cyanide, and reduced by means of alcohol and sodium to δ -phenoxybutylamine, $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OPh}$. The amine is then converted by means of benzoyl chloride into its benzoyl derivative, which, on distillation with phosphorus pentachloride, is transformed into α -chloro- δ -phenoxybutane,



Sodium iodide in alcohol then converts this chloro-ether into α -iodo- δ -phenoxybutane, $\text{CH}_2\text{I} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OPh}$, which is transformed into $\alpha\delta$ -di-iodobutane on heating with hydriodic acid at 100° for six hours.

$\alpha\delta$ -Dicyanobutane (Adiponitrile), $\text{CN} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CN}$.

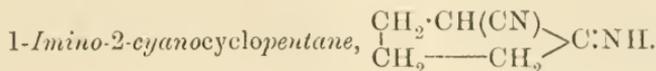
This substance was prepared by the action of alcoholic potassium cyanide on $\alpha\delta$ -di-iodobutane, the process adopted being as follows. Twenty-six grams of pure potassium cyanide were dissolved in as little water as possible, and the solution, after being mixed with three times its volume of alcohol, heated to boiling. Fifty grams of $\alpha\delta$ -di-iodobutane were then diluted with an equal volume of alcohol, heated to boiling, and gradually added to the hot alcoholic potassium cyanide. The reaction was fairly vigorous, and was completed by heating the mixture on the water-bath for one hour, when water was added to the cool solution and the precipitated oil extracted by ether. The ethereal extract was washed with water to remove alcohol, and then thoroughly shaken with dilute hydrochloric acid, being finally dried and evaporated. The residual oil was then carefully fractionated under 20 mm. pressure, and the fraction boiling at 180 — 182° collected :

0.1863 gave 0.4563 CO_2 and 0.1258 H_2O . $\text{C} = 66.78$; $\text{H} = 7.49$.

$\text{C}_6\text{H}_8\text{N}_2$ requires $\text{C} = 66.7$; $\text{H} = 7.4$ per cent.

The washing with hydrochloric acid in the above preparation was found to be necessary, owing to the production of a certain proportion of 1-imino-2-cyanocyclopentane by the alcoholic potassium cyanide. The action of hydrochloric acid converts the imino-compound into the corresponding ketone, which for the most part remains dissolved in the dilute hydrochloric acid, and can be recovered by saturating the solution with ammonium sulphate and extracting with ether. The amount of imino-compound formed in the reaction depends on the quantity of water used to dissolve the potassium cyanide. If no water is used and the interaction of the di-iodide and potassium cyanide is carried out in absolute alcohol, the formation of the imino-compound cannot be detected. The process under these conditions takes, however, a considerable time for completion, and it is advisable to employ the conditions given above and remove any imino-compound formed in the manner stated. The observation is, however, of importance, since

it shows that when potassium cyanide is used in a solvent in which it does not dissociate, the production of the imino-nitrile does not take place.



The conversion of $\alpha\delta$ -dicyanobutane into 1-imino-2-cyanocyclopentane is readily effected by boiling an alcoholic solution of the dinitrile containing a trace of sodium ethoxide. The conditions found to give the best result were as follows. Five grams of the dinitrile were mixed with 20 c.c. of absolute alcohol in a flask fitted with a reflux condenser, and a piece of clean sodium about the size of a grain of wheat added. The sodium rapidly dissolved, and the solution, which became pale yellow, was then heated on the water-bath for one hour. The imino-nitrile, which separated from the solution on cooling, was collected and purified by recrystallisation from benzene, when it was obtained in long, flattened needles, melting at 147° (compare Best and Thorpe, this vol., 709):

0.1897 gave 0.4648 CO_2 and 0.1288 H_2O . C = 66.81; H = 7.54.

$\text{C}_6\text{H}_8\text{N}_2$ requires C = 66.7; H = 7.4 per cent.

The above method was found more convenient than using a solution of sodium ethoxide in the manner described in the conversion of *o*-phenylenediacetonitrile into β -imino- α -cyanohydrindene (*loc. cit.*), although the change can be effected equally well by that means. The small amount of reduction caused by the nascent hydrogen does not apparently affect the yield of the imino-compound, which was found to be practically the same by both methods. From the 5 grams of $\alpha\delta$ -dicyanobutane used in the experiment, 4.2 grams of crude 1-imino-2-cyanocyclopentane were obtained.

The identity of the imino-compound was established by converting it, by the action of dilute hydrochloric acid, into 2-cyanocyclopentanone, and preparing the characteristic semicarbazone of this substance, which melts and decomposes at 190° (compare this vol., 709).

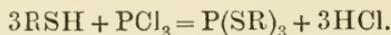
Much of the expense entailed by this research has been met by grants from the Government Grant Committee of the Royal Society, and from the Research Fund of the Chemical Society, for which I desire to express my indebtedness.

THE UNIVERSITY,
MANCHESTER.

CCXI.—*The Action of Mercaptans on Acid Chlorides.*
Part I. Oxalyl Chloride; the Mono- and Di-
*thio-oxalates.**

By HUMPHREY OWEN JONES and HUBERT SANDERSON TASKER.

THE alkyl mercaptans and their derivatives react in general with acid acid chlorides to form esters of the corresponding thio-acids; thus, for instance:



The final products of the reaction depend on the stability or instability of the ester formed, and if it is unstable, on its manner of decomposition. From the stable esters it is possible to obtain potassium salts by the action on them of alcoholic potassium hydro-sulphide, and these potassium salts have in some cases properties of special interest.

The simplest method of decomposition of phenyl thio-esters is by the elimination of phenyl disulphide, and this gives rise to the possibility of obtaining new oxides of common elements. Those salts, however, which are of this nature appear to avoid decomposition in the simple and normal manner.

Oxalyl chloride was prepared at first by a modification of the method used by Fauconnier (*Compt. rend.*, 1892, 114, 122). Two gram-molecules of phosphorus pentachloride and one gram-molecule of ethyl oxalate were heated to 150—160° in sealed tubes and the product was distilled. The fraction boiling at 70—75° contained the largest percentage of oxalyl chloride, but contained also phosphorus trichloride and phosphoryl chloride, as well as *as*-dichloroethane. Further purification, however, by distillation or precipitation of the oxalyl chloride with dry pyridine was found to be impracticable.

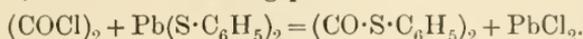
The action of sodium phenylmercaptide on oxalyl chloride was at first investigated in the hope of obtaining a new oxide of carbon, C₂O₂. No definite gaseous product, however, was obtained from the reaction, and the only solid products, apart from sodium chloride, were phenyl disulphide, triphenyl trithiophosphite, and triphenyl trithio-phosphate.

Later, oxalyl chloride was obtained pure by Staudinger's method (*Ber.*, 1908, 41, 3558), and these experiments were repeated. A

* Preliminary notes on portions of this work have already appeared (*Proc. Camb. Phil. Soc.*, 1909, 15, 94; *Proc.*, 1908, 24, 271).

small quantity of carbon monoxide was produced together with sodium chloride, phenyl disulphide in small quantity, and a substance which crystallised from alcohol in small, yellow needles.

If lead phenylmercaptide in ether suspension was used instead of the sodium salt, the reaction was less vigorous, and there was no production of gas or of phenyl disulphide, the only products being lead chloride and the yellow compound; this was presumed to be phenyl-dithio-oxalate, the reaction taking place thus:



Phenyl dithio-oxalate is best prepared by the action of one gram-molecule of oxalyl chloride on two of phenyl mercaptan. The reaction starts in the cold, and a brisk evolution of hydrogen chloride takes place. A yellow colour is produced on mixing the liquids, which eventually solidify to a crystalline, yellow mass.

On crystallisation from alcohol, sulphur-yellow, prismatic needles, melting at 119—120°, are obtained, which are readily soluble in ether or light petroleum:

0.2857 gave 0.6402 CO₂ and 0.0951 H₂O. C = 61.1; H = 3.7.

C₁₄H₁₀O₂S₂ requires C = 61.31; H = 3.65 per cent.

Treatment with hot potassium hydroxide solution converts the ester into potassium phenylmercaptide and potassium oxalate.

The ester distils unchanged under the atmospheric pressure, but is decomposed by concentrated sulphuric acid, giving carbon monoxide and a brownish-purple colour, which is a characteristic test for phenyl disulphide.

On being heated with sodium to a temperature of 200—300°, the substance chars and yields carbon monoxide.

The yellow colour of phenyl dithio-oxalate persists after repeated recrystallisation and treatment in solution with animal charcoal.

Ethyl dithio-oxalate is prepared by mixing one gram-molecule of oxalyl chloride with two of ethyl mercaptan in the cold. The liquid becomes yellow, and hydrogen chloride is evolved. The mixture is heated gently to expel any excess of either of the reacting substances, and, on cooling, sets to a yellow, crystalline mass with a characteristic and, to some, a nauseating odour. On crystallisation from ether, yellow needles are obtained, which melt at 27—27.5°, and distil unchanged at 235°; the spontaneous solidification of the crude mass thus evidences the remarkable purity of the substance. Its colour, although its existence is undeniable, is not so intense as that of the phenyl ester:

0.1826 gave 0.2694 CO₂ and 0.0883 H₂O. C = 40.3; H = 5.3.

(CO·S·C₂H₅)₂ requires C = 40.45; H = 5.6 per cent.

Methyl Dithio-oxalate.—Methyl mercaptan was passed into oxalyl chloride, when a yellow colour was produced and hydrogen chloride was evolved. On shaking the liquid with water, pale yellow crystals of methyl dithio-oxalate, melting at 81—82°, separated. In a later preparation, crystals were actually deposited from the reaction liquid, and, when crystallised from light petroleum, separated in small rhombs, melting at 82·5—83·5°. The odour of this ester is very objectionable.

Treatment with aqueous potassium hydroxide gave potassium oxalate and methyl mercaptan :

0·3211 gave 0·3755 CO₂ and 0·1179 H₂O. C = 31·9 ; H = 4·08.
(CO·S·CH₃)₂ requires C = 32·0 ; H = 4·00 per cent.

Propyl Dithio-oxalate.—This substance was prepared from oxalyl chloride and propyl mercaptan precisely in the same manner as the ethyl ester. At the ordinary temperature it is a yellow liquid boiling at 158°/15 mm. :

0·2121 gave 0·4755 BaSO₄. S = 30·8.
(CO·S·C₃H₇)₂ requires S = 31·6 per cent.

isoAmyl dithio-oxalate was prepared similarly from oxalyl chloride and *isoamyl* mercaptan. It is a yellow liquid, boiling at 206°/19 mm. :

0·2565 gave 0·4510 BaSO₄. S = 24·15.
(CO·S·C₅H₁₁)₂ requires S = 24·4 per cent.

Potassium Dithio-oxalate.—By the action of an equivalent quantity of alcoholic potassium hydrosulphide on phenyl or ethyl dithio-oxalate, also in alcoholic solution, the alkyl mercaptan is formed, and a white, crystalline precipitate of potassium dithio-oxalate is obtained, which may be collected and washed free of potassium hydrosulphide with alcohol :

0·2195 gave 0·0950 CO₂. C = 11·8.
0·1185 „ 0·2833 BaSO₄. S = 32·7.
0·2063 „ 0·1795 K₂SO₄. K = 39·01.
C₂O₂S₂K₂ requires C = 12·1 ; S = 32·3 ; K = 39·4 per cent.

This salt is very soluble in water to a yellow solution, which on evaporation on a water-bath deposits large, colourless prisms. After recrystallisation, the salt appears to become less stable, and, on keeping, turns brown with, however, no formation of sulphide.

If dilute sulphuric acid is added to a solution of potassium dithio-oxalate, hydrogen sulphide is evolved, and a yellow, amorphous solid is precipitated, which is not sulphur. The identity and properties of this substance are now under investigation.

The solution also gives the following characteristic reactions with various metallic salts :

Silver nitrate	Orange precipitate, quickly turning black.
Lead acetate	Orange precipitate, turning black on standing.
Mercurous nitrate	Black precipitate.
Mercuric chloride	Pale yellow precipitate, stable on boiling.
Bismuth nitrate	Light yellow precipitate, turning dark brown on boiling.
Cadmium chloride	Pale yellow precipitate.
Copper sulphate	Dark brown precipitate, soluble in excess of the reagent to a dark green solution. This deposits a black precipitate on boiling.
Antimony chloride.....	Yellow precipitate, turning brick-red on boiling.
Stannic ,,	Light yellow colour in the cold. On boiling, a precipitate, which turns from white to dark brown.
Stannous ,,	Reddish-brown colour, giving a dark brown precipitate on boiling.
Ferrous sulphate	A brownish-pink coloration, giving on long standing a brown precipitate.
Ferric chloride	
Zinc sulphate	Pale yellow coloration.
Nickel ,,	Deep magenta coloration which is stable on boiling. This most characteristic reaction is dealt with more fully below.
Cobalt nitrate.....	Deep reddish-brown coloration.
Manganese sulphate	Yellowish-brown coloration.
Calcium chloride	No precipitate in neutral solution. On addition of ammonia there is precipitation of calcium oxalate, sulphide remaining in solution.
Palladium chloride	Deep brown coloration. Brown precipitate on standing.
Platinous ,,	Reddish-brown coloration.
Platinic chloride and sodium carbonate	Reddish-brown coloration, deepening on standing.

It is probable that the sulphide of the heavy metal is produced in all cases where decomposition occurs on boiling.

Potassium Nickelodithio-oxalate.—Equal weights of potassium dithio-oxalate and nickel sulphate crystals were mixed in concentrated solutions. There was a copious separation of small, almost black needles, which exhibited an iridescence like that of potassium permanganate crystals. On recrystallisation from water, another form is at times obtained in dark red octahedra, the composition of which has been proved to be identical with that of the needles. The conditions necessary to the formation of the octahedra have not, however, been thoroughly determined.

A solution of these crystals does not give at once the usual tests for nickel in solution. Sodium hydroxide solution changes the colour to a greyish-brown, and nickel hydroxide precipitates only after some time. Nickel sulphide also is precipitated very slowly on addition of potassium hydrosulphide. Mercuric chloride gives a yellow precipitate, which appears to be mercuric dithio-oxalate, leaving nickel in solution.

These facts suggest that the substance is potassium nickelodithio-oxalate, and the structural formula $KS \cdot CO \cdot CO \cdot S \cdot Ni \cdot S \cdot CO \cdot CO \cdot SK$ is suggested :

0.2097 gave 0.0979 CO_2 . C = 12.78.

0.1974 ,, 0.4960 BaSO_4 . S = 34.4.

$\text{C}_4\text{O}_4\text{S}_4\text{K}_2\text{Ni}$ requires C = 12.74 ; S = 34.0 per cent.

It is probable that those metals (iron and cobalt) which give similar colorations with potassium dithio-oxalate form compounds of the same type. These, however, are very soluble, and do not crystallise so well as does the nickel compound.

The sensitiveness of these colours as tests for the presence in solution of iron, nickel, cobalt, or dithio-oxalate was determined.

The colour effect can be used to detect nickel at a dilution of one part of nickel in 40,000,000 of water if sufficient of the solution is used to fill a large beaker, and one part in 8,000,000 can be detected readily in a test-tube. The colour is about three times as intense as that of potassium permanganate, and half as intense as that of rosaniline, if the concentrations are calculated weight for weight.

The cobalt coloration is just as intense as that of nickel, and at a dilution of one part of cobalt in 4,000,000 is about identical with the colour produced by the addition of potassium thiocyanate to a solution of ferric chloride containing one part of iron in 400,000. It will therefore be seen that the formation of these colorations constitutes a test remarkably delicate in consideration of the fact that they depend on the formation of a complex ion in dilute solution.

The iron coloration was just perceptible at a strength of 1 in 100,000 of iron.

The nickel coloration could be detected in a solution of potassium dithio-oxalate of the strength of 1 in 100,000.

The cobalt salt is much more stable than that of nickel. It decomposes on standing in solution much more slowly, and the coloration is comparatively little destroyed by the addition of hydrochloric acid or potassium cyanide. The nickel coloration, on the other hand, is destroyed slowly by dilute hydrochloric acid, but at once by excess of concentrated acid. Potassium cyanide also quickly discharges it.

This fact makes it possible to detect cobalt in a mixture containing 10 per cent. of cobalt and 90 per cent. of nickel. On adding potassium dithio-oxalate to the solution, a deep purple coloration is obtained, but on addition of excess of potassium cyanide the purple coloration disappears and the solution remains brown.

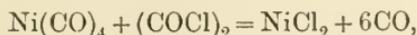
It will be seen from statements made above that the presence of iron does not interfere with the detection of nickel and cobalt in dilute solutions.

Ammonium dithio-oxalate is prepared by the action of alcoholic ammonium hydrosulphide on phenyl dithio-oxalate. It is a crystalline solid, which gives the characteristic tests for dithio-oxalates, but is decomposed by heating its solution on the water-bath.

It may be conveniently mentioned here that, with the preparation of the compound C_2O_2 as object, the action of nickel carbonyl on oxalyl chloride was examined. When the substances react in the liquid state, the evolution of gas is very rapid, and the reaction mixture falls in temperature.

The gas evolved appears to be carbon monoxide, and nickel chloride is deposited. This was confirmed by allowing the substances to react in the gaseous state. Two bulbs of equal volume, each surrounded by a bath and each connected with a mercury manometer, were respectively filled with the vapours of nickel carbonyl and oxalyl chloride. The bulbs were connected by a tube fitted with a tap, which was closed before the bulbs were filled. The pressure in each bulb having been noted, the tap was opened, and the gases thus allowed to mix. The pressure was read from time to time, until it ceased to increase.*

If the reaction takes place in accordance with the equation



the final pressure will be three times as great as the initial pressure.

Two experiments, in which the following results were obtained, may be quoted as typical:

Pressure of vapour of $Ni(CO)_4$.	Pressure of vapour of $(COCl)_2$.	Final pressure.
34 mm.	39 mm.	109 mm.
52 ,,	59 ,,	158 ,,

Thus it seems that the above equation represents the course of the reaction, and hence it may be concluded that the C_2O_2 formed momentarily is so unstable that it at once decomposes to give two molecules of carbon monoxide in the cold.

The colour and other optical properties of the compounds here described and of other sulphur compounds are being investigated.

The expenses of this investigation were partly defrayed by a grant from the Government Grant Committee of the Royal Society, for which the authors are glad to make this grateful acknowledgment.

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

* This apparatus is convenient for the investigation of reactions between vapours, and will be described more fully in another communication.

CCXII.—*The Action of Mercaptans on Acid Chlorides.*
Part II. The Acid Chlorides of Phosphorus,
Sulphur, and Nitrogen.

By HUBERT SANDERSON TASKER and HUMPHREY OWEN JONES.

THE presence of phosphorus trichloride and phosphoryl chloride in crude oxalyl chloride resulted, as has been shown in the preceding paper, in the formation of triphenyl trithiophosphite and triphenyl trithiophosphate when the liquid was allowed to react with sodium phenylmercaptide.

Schwarze (*J. pr. Chem.*, 1874, [ii], 10, 222) claimed that he obtained triphenyl trithiophosphate by the action of phosphoryl chloride on phenyl mercaptan, ascribing to it the melting point 72°.

Michaelis (*Ber.*, 1907, 40, 3419) has investigated the properties of triphenyl trithiophosphite and triphenyl trithiophosphate, and finds that their melting points are 77° and 115° respectively. He suggests that Schwarze's product was merely phenyl disulphide. If this be so, as is improbable, for the melting point of phenyl disulphide is 61°, it becomes likely that the reaction may give an interesting reduction product of phosphoryl chloride, thus:



This point has been investigated, and results seem to show that Michaelis's surmise was incorrect, although his general results were confirmed. Incidentally, it was found that triphenyl trithiophosphite can be oxidised to triphenyl trithiophosphate by potassium dichromate and sulphuric acid, or by nitric acid. It forms no additive product with methyl iodide or hydrogen chloride. The interaction of phenyl mercaptan and phosphoryl chloride in molecular proportions at 100° resulted in the production of a mixture of triphenyl trithiophosphate and phenyl disulphide. The two products could be completely separated by crystallisation from alcohol. All attempts to isolate the hypothetical compound POCl failed, and it is probable that phenyl disulphide is formed in the reduction of phosphoryl chloride to phosphorus trichloride, thus:

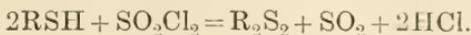


The water would then form phosphoric acid with the excess of phosphoryl chloride, and the phosphorus trichloride would probably be carried off at the temperature of the reaction in the streams of hydrogen chloride which are evolved.

It thus seems probable that Schwarze's compound was triphenyl trithiophosphate, as his analyses go to prove, the low melting point being accounted for by the contamination with phenyl disulphide.

The Acid Chlorides of Sulphur.

Holmberg (*Annalen*, 1908, **359**, 81) has stated that sulphuryl chloride reacts with alkyl mercaptans to give the corresponding alkyl disulphide, sulphur dioxide, and hydrogen chloride, thus:

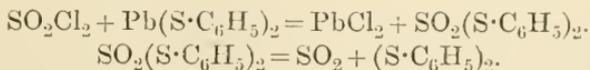


This result has been confirmed for phenyl mercaptan. By using lead phenylmercaptide, however, or phenyl mercaptan in ethereal solution, evidence was obtained for the transitory existence of an unstable phenyl dithiosulphate.

Sulphuryl chloride in ethereal solution was added to lead phenylmercaptide at the ordinary temperature. Sulphur dioxide was evolved at once, and the residue was found to consist of lead chloride and phenyl disulphide.

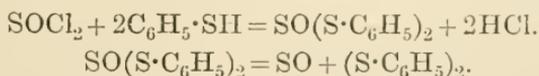
When, however, the reaction was carried out in a freezing mixture, the formation of lead chloride was detected by the change in colour of the lead phenylmercaptide, but the solution became reddish-yellow, and no gas was evolved. On warming the solution, however, or allowing it to evaporate, the colour disappeared, sulphur dioxide and phenyl disulphide being obtained.

There seems little doubt that phenyl dithiosulphate is formed in solution, but it was found impossible to isolate it. The reaction could then be represented thus:



The behaviour was similar when an ethereal solution of phenyl mercaptan reacted with sulphuryl chloride at low temperatures.

These considerations made the study of the behaviour of thionyl chloride with phenyl mercaptan and its derivatives one of especial interest, for an analogous reaction might be expected to give rise to a new oxide of sulphur, SO, thus:



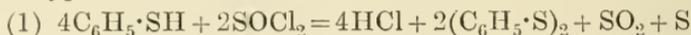
The expectation, too, was strengthened by the fact that a similar but paler transient colour was noticed when phenyl mercaptan or lead phenylmercaptide was allowed to react with thionyl chloride in ethereal solution at a low temperature.

The gaseous products of the reaction were therefore subjected to examination.

One gram-molecule of thionyl chloride was allowed to react with two of phenyl mercaptan at 0° or at other temperatures down to -70°, and the gases evolved were swept by means of a stream of

dry hydrogen through U-tubes cooled to -70° , so that the gases might be liquefied.

Hydrogen chloride was obtained, and sulphur dioxide was detected in large quantity, both by its odour and by its boiling point. This indicated that the decomposition of thionyl chloride involves the participation of more than one molecule, and the simplest hypotheses for the reaction become:



and



The latter hypothesis would involve the formation of another new oxide of sulphur, S_2O .

The reduction of thionyl chloride by nickel carbonyl was found to throw light on the problem by analogy. These substances interact vigorously in the cold; sulphur dioxide and carbon monoxide are evolved, and a brown mass remains which consists of nickel chloride and sulphur—it being possible to extract the latter by solution in carbon disulphide. The reaction, although so vigorous, lowered the temperature of the reaction mixture.

It was found impossible, however, in the case of the reaction with phenyl mercaptan to extract sulphur from the residue.

It was therefore decided to collect the gases evolved, and to determine their total acidity, and also the extent to which they could reduce iodine.

4.1 Grams of thionyl chloride were allowed to react with 7.3 grams of phenyl mercaptan in a distilling flask at a low temperature. The gases evolved were swept by means of a stream of dry hydrogen through an empty wash-bottle and two U-tubes into 200 c.c. of *N*-sodium hydroxide solution.

It was possible, by surrounding the U-tubes with freezing mixtures, to estimate approximately the boiling points of the gases evolved.

When violent reaction had ceased, the temperature of the reaction flask was raised until the residue melted and ceased to evolve gas. The residue at 60° was a clear, yellow liquid, which deposited phenyl disulphide on cooling. This could be collected, and the viscous liquid so obtained continued for some time to deposit small quantities of phenyl disulphide.

In addition to this yellow oil and phenyl disulphide, there appeared drops of a less dense and more mobile liquid, which was identified as water by the coloration of anhydrous copper sulphate and by its action on sodium. It seemed to be a product of the reaction, for it invariably appeared in spite of special precautions which were taken to dry the hydrogen used. Its

amount could not be estimated, owing to the small quantity formed, and the large excess of the other residual products.

By cooling the U-tubes, hydrogen chloride and sulphur dioxide were identified by their boiling points, but there was no evidence of any other volatile product boiling above -70° .

The sodium hydroxide solution was titrated first with *N*/10-sulphuric acid, and then with *N*/10-silver nitrate, to determine the amount of hydrogen chloride evolved. Sulphur dioxide was estimated by titration of the neutral solution with standard iodine solution.

Two experiments were made, and the quantity of hydrogen chloride estimated differed by only 2 per cent., showing that the gases were thoroughly swept out of the apparatus. As a mean of the two experiments, 2.55 grams of hydrogen chloride and 0.777 gram of sulphur dioxide were produced by the interaction of 4.1 grams of thionyl chloride and 7.3 grams of phenyl mercaptan.

The first hypothetical equation demands 2.45 grams of hydrogen chloride and 1.06 grams of sulphur dioxide, whilst the second requires 2.45 grams of hydrogen chloride and 0.71 gram of sulphur dioxide.

Low, rather than high, readings would be expected, and the fact that the sulphur dioxide results are relatively high tends to discountenance the validity of the second equation.

In these equations, too, the possible presence and volatility of the compound S_2O has been ignored. Its presence would be expected at least to double the power of the products to reduce iodine, so that the observed reading would fall very far short of that required.

Nor did the solution on qualitative examination show any evidence for the existence in it of a salt corresponding with a new oxide of sulphur.

Examination of the residual mass gave further evidence in support of the first equation.

The liquid obtained after collecting the phenyl disulphide which separated was distilled under diminished pressure. Between 180° and $220^{\circ}/10$ mm. phenyl disulphide distilled over, and an amorphous, sticky, brown mass remained behind. Phenyl disulphide, when distilled alone, does not decompose, and leaves no residue.

Analyses of two specimens of the liquid gave the following results:

0.2203 gave 0.4005 CO_2 and 0.0710 H_2O . C=49.57; H=3.3.

0.2112 „ 0.3890 CO_2 „ 0.0650 H_2O . C=50.0; H=3.42.

$(C_6H_5)_2S_4$ requires C=51.1; H=3.55 per cent.

$(C_6H_5)_2S_3$ „ C=57.6; H=4.0 „

It seemed probable that the liquid is either phenyl tetrasulphide which still holds a little phenyl disulphide in solution, or else a difficultly crystallisable solution of sulphur in phenyl disulphide.

Phenyl tetrasulphide is described as a viscid, yellow oil, which decomposes on distillation into sulphur and phenyl disulphide. The properties of the oil obtained closely correspond with these.

A solution of sulphur in phenyl disulphide in the proportions corresponding with $(C_6H_5)_2S_4$ was prepared. It solidified, on cooling, to a hard, cream-coloured mass, the appearance of which had nothing in common with that of the liquid obtained from the reaction.

Thus an equation can be written to include the phenyl tetrasulphide which seems to be formed:



In support of this, it was found that 14.6 grams of phenyl mercaptan and 8 grams of thionyl chloride produced 10.65 grams of phenyl disulphide, whilst the above equation requires 11.27 grams.

Thus the equation represents the reaction fairly well, except for the water, a small quantity of which is invariably formed.

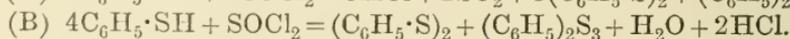
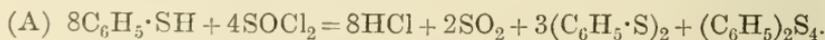
At this point our attention was drawn to a statement by Holmberg (*loc. cit.*), to the effect that alkyl mercaptans react with thionyl chloride in accordance with the general equation:



This hypothesis accounts for the formation of water, but takes no account of the evolution of sulphur dioxide, and since phenyl trisulphide is a solid, it would demand that the residual mass should become completely solid at the ordinary temperature. Reference to the experiments already quoted suggested that the two reactions might proceed simultaneously, for sulphur dioxide was always produced in quantity smaller than that required by the equation proposed.

Further experiments were devised to ascertain whether either of the two hypotheses correctly represents the reaction under any special conditions.

It will be convenient if the two equations be henceforth referred to as A and B, thus:



A weighed quantity of thionyl chloride was allowed to react with an excess of lead phenylmercaptide in a U-tube. A continual stream of dry air, freed from carbon dioxide, swept the gases

evolved into a measured volume of standard sodium hydroxide solution. After sweeping with air for eight hours, it was found that no more gas was absorbed by the alkali. The sodium hydroxide solution was neutralised and titrated with standard iodine to estimate the sulphur dioxide, when it was found that 1.955 grams of thionyl chloride gave 0.473 gram of sulphur dioxide. If thionyl chloride is decomposed in accordance with equation A, 0.526 gram of sulphur dioxide should be evolved. In this case, by the use of a metallic derivative of phenyl mercaptan, the formation of water as demanded by equation B was prevented. The satisfactory agreement obtained (considering the nature of the experiment) indicates that in this case a modification of equation A would adequately represent the reaction.

Unfortunately, an experiment of similar nature with phenyl mercaptan itself, in place of the lead derivative, was found to be impracticable, for the stream of air carries over into the sodium hydroxide considerable quantities of that one of the reactive liquids which happens to be present in excess. Another method was therefore devised.

The hydrogen chloride and sulphur dioxide produced were estimated by heating the total products of the reaction with a measured excess of standard alkali and by titration of the solution obtained. The two liquids were weighed, and the effect of an excess of either on the titrations was allowed for.

The suitability of the method for discrimination between equations A and B depends on the proportions of the reacting substances used. The proportion of 8 gram-molecules of phenyl mercaptan to 4 gram-molecules of thionyl chloride demands, according to A, 12 equivalents of alkali and 4 equivalents of iodine, and exactly the same quantities are required according to B. Thus, if the substances are used in this proportion, no discriminative result will be obtained. A more decisive result can be obtained by using 16 gram-molecules of phenyl mercaptan to 4 of thionyl chloride. Equation A will then require 20 equivalents of alkali and 12 of iodine (one gram-molecule of phenyl mercaptan neutralises one gram-molecule of sodium hydroxide, and reduces one gram-atom of iodine), whilst B will require 8 equivalents of alkali and no iodine.

This was the proportion used in the experiments. Standard solutions of phenyl mercaptan and of thionyl chloride in dry ether were made. The required volume of each was measured into a stoppered bottle, and the bottle was shaken from time to time. A measured excess of *N*-sodium hydroxide solution was then added, and, after further shaking, the whole was titrated, first with acid, and then

with iodine. Preliminary experiments proved that the titrations were sufficiently accurate under these conditions. Two experiments may be quoted to illustrate the results obtained.

	Thionyl chloride, gram.	Phenyl mercaptan, gram.	Readings.	Equation <i>A</i> requires	Equation <i>B</i> requires
1.	0.178	0.664	7.1 c.c. <i>N</i> -alkali 0.477 gram iodine	7.5 c.c. 0.573 gram	3.0 c.c. —
2.	0.171	0.632	5.8 c.c. <i>N</i> -alkali 0.395 gram iodine	7.15 c.c. 0.515 gram	2.85 c.c. —

These results seem to indicate that both reactions, represented by equations *A* and *B*, take place simultaneously.

In order to carry out the same type of experiment, using the pure substances instead of the ethereal solutions, a special device was adopted.

One of the substances was weighed into a large flask fitted with two tap funnels, one small and the other large. The small funnel, containing about the right amount of the other substance, was weighed before the reaction, and weighed again when the reaction was over and the liquid had been allowed to enter the flask. The large funnel contained 100 c.c. of *N*-sodium hydroxide solution. The liquid in the small funnel was allowed to run by small instalments into the flask, the evolved gases being allowed to escape through the alkali in the large funnel so as to absorb all the hydrogen chloride and sulphur dioxide.

The pressure in the flask was easily regulated by heating and cooling. The reaction being quite finished, the sodium hydroxide solution was allowed to run into the flask, and the contents were shaken. The solution was then filtered through glass wool, made up to 200 or 250 c.c., and titrated with acid and iodine.

The results obtained are expressed, as before, in grams of iodine required to oxidise the sulphur dioxide and phenyl mercaptan and in c.c. of *N*-acid required to neutralise the sulphur dioxide, phenyl mercaptan, and hydrogen chloride produced. The theoretical amounts are calculated by finding the amount of alkali

	Thionyl chloride, grams.	Phenyl mercaptan, grams.	Readings.	Equation <i>A</i> requires	Equation <i>B</i> requires
1.	1.984	1.742	54.8 c.c. <i>N</i> -alkali 2.51 grams iodine	59.0 c.c. 3.652 grams	58.8 c.c. 3.23 grams
2.	0.878	3.408	22.4 c.c. <i>N</i> -alkali 1.13 grams iodine	38.4 c.c. 2.99 grams	16.3 c.c. 0.205 gram
3.	2.186	5.477	59.5 c.c. <i>N</i> -alkali 2.75 grams iodine	68.2 c.c. 3.6 grams	48.6 c.c. 1.5 grams
4.	1.0105	3.63	25.0 c.c. <i>N</i> -alkali 0.85 gram iodine	41.5 c.c. 3.11 grams	17.1 c.c. 0.04 gram

or iodine required by the reaction products (the reaction is assumed to use up the substance not present in excess), and by adding to these values the amounts required by the excess of the other reacting substance.

The first experiment serves to show the limited accuracy of the method, the calculated results being about the same for each equation.

In the other cases, the observed value is always intermediate between the two calculated values, and if a rough correction be made for the losses as observed in experiment 1, the experimental values are found to give the balance of evidence in favour of equation A.

In experiments 2 and 4, the proportions taken are about those demanded for equation B₂, and in these cases the reaction seems to follow this equation to a greater extent than in 3, where there is a larger proportional amount of thionyl chloride.

It is unfortunate that the addition of a further amount of thionyl chloride renders the method no longer discriminative.

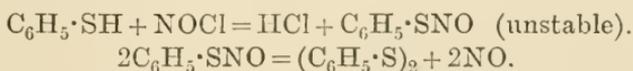
It must be concluded that the two different reactions take place simultaneously. The proportions in which the reacting substances are present may be one of the factors which determine the ratio of the extents to which the two reactions proceed.

Nitrosyl Chloride.

The behaviour of nitrosyl chloride with mercaptans is apparently analogous to that of sulphuryl chloride.

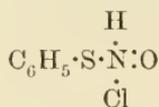
When nitrosyl chloride is passed into phenyl mercaptan, the liquid turns port-wine red, and hydrogen chloride is evolved. The nitrosyl chloride is completely absorbed by the mercaptan, but the coloured liquid rapidly evolves nitric oxide. If the introduction of nitrosyl chloride is stopped, the colour gradually disappears with slower and slower evolution of nitric oxide, and phenyl disulphide finally separates out.

It would thus appear that the coloured and unstable phenyl thionitrite is formed in solution, and that this decomposes to give the final products of the reaction, thus:



It is, however, possible that the colour may be due to a direct additive product of phenyl mercaptan and nitrosyl chloride. To test this, nitrosyl chloride was allowed to react with an ethereal suspension of lead phenylmercaptide. The red colour was again

produced, and lead chloride was left in suspension. Thus, a compound such as



cannot be responsible for the colour of the solution.

The unstable, intermediate product may be preserved some time if the solution is kept at a low temperature, but all attempts to isolate it failed.

The corresponding ethyl and methyl compounds were obtained in solution.

On passing nitrosyl chloride into an ethereal suspension of mercury methylmercaptide, $\text{Hg}(\text{S} \cdot \text{CH}_3)_2$, the liquid became brownish-pink, and mercuric chloride was formed. The colour rapidly disappeared on standing and nitric oxide was evolved.

This behaviour is quite analogous to that observed in the case of lead phenylmercaptide.

The action of ethyl mercaptan on nitrosyl chloride at a low temperature resulted at first quite normally in the formation of a magnificent cherry-red colour, and in the evolution of hydrogen chloride. The red colour eventually disappeared with evolution of nitric oxide. In a freezing mixture of solid carbon dioxide dissolved in ether, however, a white, crystalline solid was deposited in small quantity. This was separated from the solution and re-crystallised from alcohol. It was eventually identified as hydroxylamine hydrochloride, and must be the product of a side-reaction involving the reduction of the nitrosyl chloride.

The unstable, coloured thionitrites show two absorption bands, one sharply defined and broad in the yellowish-green, and the other narrower and diffuse in the green portion of the spectrum. The substitution of an alkyl group of high molecular weight for one of low molecular weight shifts the bands towards the red end of the spectrum.

The expenses of this investigation were partly defrayed by a grant from the Government Grant Committee of the Royal Society, for which the authors are glad to make this grateful acknowledgment.

CCXIII.—*Contributions to the Theory of Solutions.*

By JOHN HOLMES and PHILIP JOHN SAGEMAN.

THE nature of the forces operative in solution, and more particularly in aqueous solution, has, in recent years, been the subject of much experimental investigation on the part of both chemists and physicists. A critical survey of the theories which have from time to time been put forward to explain the property of solution leaves, however, much to be desired, and leads to the conclusion that they severally afford only plausible explanations for a narrow circle of phenomena, and are incapable of general application.

Of these theories, the two which are by far the most important are the "Hydrate theory," first promulgated by Mendeléeff, and the "Dissociation theory" of Arrhenius.

Mendeléeff attempted to explain the phenomena peculiar to aqueous solutions by the production and subsequent dissociation of hydrates at different concentrations. With the advent of cryoscopic methods of determining molecular weights, and the interpretation of the results of electrical conductivity experiments by Arrhenius, the "Hydrate theory" fell for a time into disrepute, but recently it has in a modified form received such support that Findlay (*Ann. Reports*, 1907, **4**, 21) states that "hydrate formation is now accepted probably by the majority of physical chemists."

Solution in water, therefore, which almost invariably results in a marked contraction in volume, is generally regarded as being of the nature of combination, and hydration of the molecules of the dissolved substance increases with the dilution (Jones and Uhler, *Amer. Chem. J.*, 1907, **37**, 126, 244).

The endeavours of the many investigators in this field are far from conclusive, however, regarding the existence of such complexes, and much contradictory evidence from widely different sources is forthcoming in this connexion. For instance, Morse, Frazer, and Lovelace (*Amer. Chem. J.*, 1907, **37**, 360) conclude, from cryoscopic work on aqueous dextrose solutions, that, even at the freezing point, dextrose exists in the anhydrous condition, and does not combine with the solvent. Kremann and Kerschbaum (*Monatsh.*, 1907, **28**, 911), from a consideration of the specific heat of the mixture $\text{H}_2\text{SO}_4 - \text{H}_2\text{O}$ on cooling through a wide range of temperature, conclude that the heat developed on mixing must be ascribed to other causes than to the formation of a hydrate of sulphuric acid. Similar conclusions are drawn in the case of sodium sulphate in aqueous solution by Marie and Marquis (*Compt. rend.*, 1903, **136**,

684) from the continuous solubility curves given by solutions of sodium chloride in aqueous sodium sulphate at temperatures including the transition temperatures of crystallised sodium sulphate in water and in sodium chloride solutions. Perman also deduces the non-existence of hydrated complexes in aqueous solutions of sodium sulphate and potassium sulphate from the results of experiments on the influence of these salts on the vapour pressure of aqueous ammonia solutions (Trans., 1902, **81**, 489).

Apart from such anomalies, however, a hydrate theory affords but little assistance in explaining the varied properties of other than aqueous mixtures, which represent only one branch of the problem of solution, and in order to arrive at a better understanding of these forces, it is necessary to seek other explanations of the same phenomena.

According to Arrhenius (*Zeitsch. physikal. Chem.*, 1887, **1**, 631), the molecular condition of a dissolved salt must be regarded as that of a more or less dissociated substance, and the properties of salt solutions are considered to be consistent with the presence of free ions. The molecular conductivity of such solutions increases with the dilution, and, according to this theory, the degree of dissociation can be calculated from the electrical conductivity or the results of cryoscopic molecular weight determinations. Arrhenius's theory has been subjected to much adverse criticism in recent years, and many experimental results are deemed irreconcilable with the theory of ionic dissociation (see Kahlenberg, *J. Physical Chem.*, 1901, **5**, 339, and *Trans. Faraday Soc.*, 1905, **1**, 42; Armstrong, *Proc. Roy. Soc.*, 1907, A, **79**, 586; 1908, A, **81**, 80; Lincoln, *J. Physical Chem.*, 1899, **3**, 457; and others). The most important objection to the theory is its failure to interpret the case of concentrated solutions, together with the fact that it is untenable in the case of non-aqueous mixtures.

It may not be permissible to apply the laws which are valid for gases to non-gaseous substances, but there is no reason for assuming that the forces which determine the coherence of the molecule in the several states of aggregation differ otherwise than in degree. Under constant conditions of temperature and pressure, and in the absence of chemical change, the gaseous molecule retains its individuality when mixed with other gaseous molecules, and the breaking down of molecular complexes and ionic dissociation on admixture in this the simplest state of aggregation are equally unnecessary for the explanation of gaseous phenomena.

According to the electrical theory of the constitution of matter, the atom is never electrically neutral, and the phenomena appertaining to electrically charged bodies may be expected to occur

between the nuclei of different atoms. In these circumstances, the molecule, which is a congeries of such atoms, must also be electrically active, and may be regarded as consisting of a nucleus of great density, in which the atoms composing the molecule are swayed and controlled with mathematical precision in their several orbits according to the intensity of their respective electrical charges; the resultant of these several interacting forces would, in the case of similar molecules, create an atmosphere or sphere of influence (the molecular co-volume of Traube, *Ber.*, 1907, **40**, 723, 736), the extent of which will depend on the magnitude of the resultant, and the consequent repulsive force operative between adjacent envelopes. It is reasonable to suppose that the equilibrium thus determined would remain constant under similar conditions, but at once be disturbed by admixture with molecules of different electrical constitution, and possessing maybe a greater or less sphere of influence. If the attractive force between different molecules in a mixture is so great as to cause the rupture of the intervening envelopes, a molecule with wholly different properties will be formed, whose sphere of activity will be dependent on the latent resultant force of the new atomic arrangement, but so long as no chemical change occurs, the molecules in a mixture may be expected to retain their respective individualities—the only change consequent on mixing being an increase or decrease in the initial volumes resulting from the new conditions of equilibrium necessitated by the interaction of differently electrified bodies, and a readjustment of the dimensions of the interspaces.

In the gaseous state of aggregation, the individual molecules are so far removed from the sphere of action of their neighbours that they are scarcely influenced by molecular forces, and obey the general laws of mechanics. Gases alone, for instance, possess the property of unlimited intermiscibility, and the physical properties of a gaseous mixture can be deduced within a near approach to accuracy from the properties of the several ingredients. The gaseous laws are, however, only approximate, and the pressure exerted by a gaseous mixture does not always rigidly accord with the sum of the initial pressures.

It is common knowledge, however, that in the case of liquids and solutions there is associated with the intermingling a change in the properties belonging to the constituents of the mixture, and not only does the volume of the mixture invariably differ from the sum of the initial volumes, but the specific rotation, specific heat, refractive index, and other physical properties are not strictly additive. The change in volume is perhaps capable of determination with greater precision than is the case with other physical

properties, and it is from a study of these deviations from simple additive relations that we hope to gain information concerning the nature of the forces operative in solution, and the correlation of physical properties with molecular structure.

The importance of change in volume in this connexion was noticed as long ago as 1865 by Bussy and Buignet (*Ann. Chim. Phys.*, [iv], 4, 5), and they record the fact that the mixing of liquids results in both volumetric and temperature changes, which may be positive or negative according to the nature of the constituents of the mixture. Various mixtures of liquids have been investigated by Brown (*Trans.*, 1881, 39, 202), Guthrie (*Phil. Mag.*, 1884, [v], 18, 495), Linebarger (*Amer. J. Sci.*, 1896, [iv], 2, 226; see also *Amer. Chem. J.*, 1896, 18, 440), Thorpe and Rodger (*Trans.*, 1897, 71, 367), and others, but apart from the fact that certain forces are operative between heterogeneous molecules, no definite conclusions have been drawn regarding the nature or magnitude of these forces. It is evident, however, from the experimental results that the molecules which make up the mass of a substance in the liquid state are capable of occupying a different volume, and as regards their mean distances from each other are in a position of relative equilibrium liable to change when the forces which influence them change.

The behaviour of acetone and *n*-propyl alcohol in aqueous solution affords important evidence in this direction. There is reason to believe that these liquids are similarly associated (see *Trans.*, 1906, 89, 1781), and have in consequence almost identical molecular weights and molecular volumes. In these circumstances, if the volumetric changes were conditioned only by an adjustment of spacing due to differences in the volumes of the respective molecules, it would be expected that the change in volume occurring in aqueous mixtures of these liquids would be of the same magnitude. The fact that acetone yields with water a contraction in volume in amount almost twice that obtained in corresponding mixtures of *n*-propyl alcohol proves, if we admit similar association, that not only do intermolecular spaces exist, but that each molecule contains a fixed amount of electrical energy, or is subject to some combination of circumstances which assumes all the appearances of electrical energy.

A theory regarding the condition of substances in solution as a regular arrangement of molecules in a comparative state of rest, each possessing within its sphere of activity latent positive and negative electrical affinities, was first promulgated by Grotthüss to explain the phenomena of electrolysis. The complete abandonment of this theory, and also of the electrochemical theory of

Berzelius, by chemists renders a reintroduction of similar hypotheses difficult, and justifiable only in so far as they are capable of affording explanations of common phenomena which are not forthcoming in the case of existing theories.

Our present object is to develop, in the direction already indicated, the electrical theory of matter as applied to the liquid state of aggregation, and endeavour to establish the entity of the liquid molecule under normal conditions.

Volume Changes Accompanying Chemical Change.

Before proceeding to a consideration of the forces operative in mixtures of liquids, it seemed desirable further to investigate (see Trans., 1907, 91, 1608) the nature of the volumetric changes occurring in aqueous mixtures in which these changes can be referred to the action of chemical forces.

According to the electrical theory of the nature of the molecule, the volume change can no longer be attributed to forces inherent in the molecules of the initial constituents of the mixture, but will be dependent on the physical nature and behaviour of the compounds formed. When an alkali is neutralised by an acid, for instance, the resulting volume of the mixture is conditioned only by the solution volume of the resulting salt, and this change may be positive or negative according to the nature of the salt. It is found that, although the admixture in aqueous solution of many acids, such as sulphuric acid, phosphoric acid, and oxalic acid, with their salts, results in a marked change in volume, the corresponding change occurring when the same salts are mixed with the basic hydrates is so small as to be negligible, in comparison with the relatively large volumetric changes obtained on neutralisation.

The following mixtures were made with the object of ascertaining the nature of the change in volume resulting from a gradual neutralising of basic hydrates with various acids in dilute aqueous solution. The densities of the different solutions and mixtures were determined at 15°/15° in a pycnometer having a capacity of about 70 c.c., and the change in volume is calculated from the several weights and densities.

(i) *Mixtures of Aqueous Sodium Hydroxide and Sulphuric Acid (approx. normal).*

Density of sodium hydroxide solution = 1.04376.
 ,, sulphuric acid ,, = 1.03209.

Equivalent volumes 100NaOH aq. : 100H₂SO₄ aq.

Volume of sodium hydroxide solution.	Volume of sulphuric acid solution.	Increase in volume after mixing.
100	16.50	+ 0.195
100	20.22	0.239
100	33.02	0.390
100	49.50	0.589
100	81.12	0.973
100	99.26	1.198
100	198.96	1.518

(ii) *Mixtures of Aqueous Potassium Hydroxide and Hydrochloric Acid (approx. normal).*

Density of potassium hydroxide solution = 1.05001.
 ,, hydrochloric acid ,, = 1.01793.

Equivalent volumes 100KOH aq. : 100HCl aq.

Volume of potassium hydroxide solution.	Volume of hydrochloric acid solution.	Increase in volume after mixing.
100	16.75	+ 0.311
100	33.16	0.632
100	66.90	1.309
100	100.46	2.001
100	150.40	2.027

(iii) *Mixtures of Aqueous Ammonia and Hydrochloric Acid (approx. normal).*

Density of ammonia solution = 0.99270.
 ,, hydrochloric acid ,, = 1.01794.

Equivalent volumes 100NH₃ aq. : 100HCl aq.

Volume of ammonia solution.	Volume of hydrochloric acid solution.	Decrease in volume after mixing.
100	19.12	- 0.123
100	33.44	0.215
100	66.68	0.431
100	100.09	0.644
100	150.40	0.644

(iv) *Mixtures of Aqueous Barium Hydroxide and Hydrochloric Acid (approx. 3/10-normal).*

Density of barium hydroxide solution = 1.02840.
 ,, hydrochloric acid ,, = 1.00555.
 Equivalent volumes 100Ba(OH)₂ aq. : 100HCl aq.

Volume of barium hydroxide solution.	Volume of hydrochloric acid solution.	Increase in volume after mixing.
100	16.72	+ 0.101
100	33.41	0.204
100	66.36	0.404
100	99.97	0.613
100	150.24	0.616

(v) *Mixtures of Aqueous Sodium Hydroxide and Acetic Acid (approx. normal).*

Density of sodium hydroxide solution = 1.04377.
 ,, acetic acid ,, = 1.00908.
 Equivalent volumes 100NaOH aq. : 99.2C₂H₄O₂ aq.

Volume of sodium hydroxide solution.	Volume of acetic acid solution.	Increase in volume after mixing.
100	17.02	+ 0.157
100	33.87	0.329
100	67.01	0.659
100	100.95	1.007
100	150.41	1.601

(vi) *Mixtures of Aqueous Sodium Hydroxide and Tartaric Acid (approx. normal).*

Density of sodium hydroxide solution = 1.04376.
 ,, tartaric acid ,, = 1.03391.
 Equivalent volumes 100NaOH aq. : 100.4C₄H₆O₆ aq.

Volume of sodium hydroxide solution.	Volume of tartaric acid solution.	Increase in volume after mixing.
100	17.30	+ 0.160
100	33.70	0.313
100	67.56	0.641
100	101.30	0.974
100	151.50	1.016

(vii) *Mixtures of Aqueous Sodium Hydroxide and Oxalic Acid.*

Density of sodium hydroxide solution = 1.04376.
 (a.) ,, oxalic acid ,, = 1.02621.
 Equivalent volumes 100NaOH aq. : 82.5H₂C₂O₄ aq.

Volume of sodium hydroxide solution.	Volume of oxalic acid solution.	Increase in volume after mixing.
100	20.74	+ 0.251
100	41.08	0.502
100	81.93	1.014
100	101.25	1.150

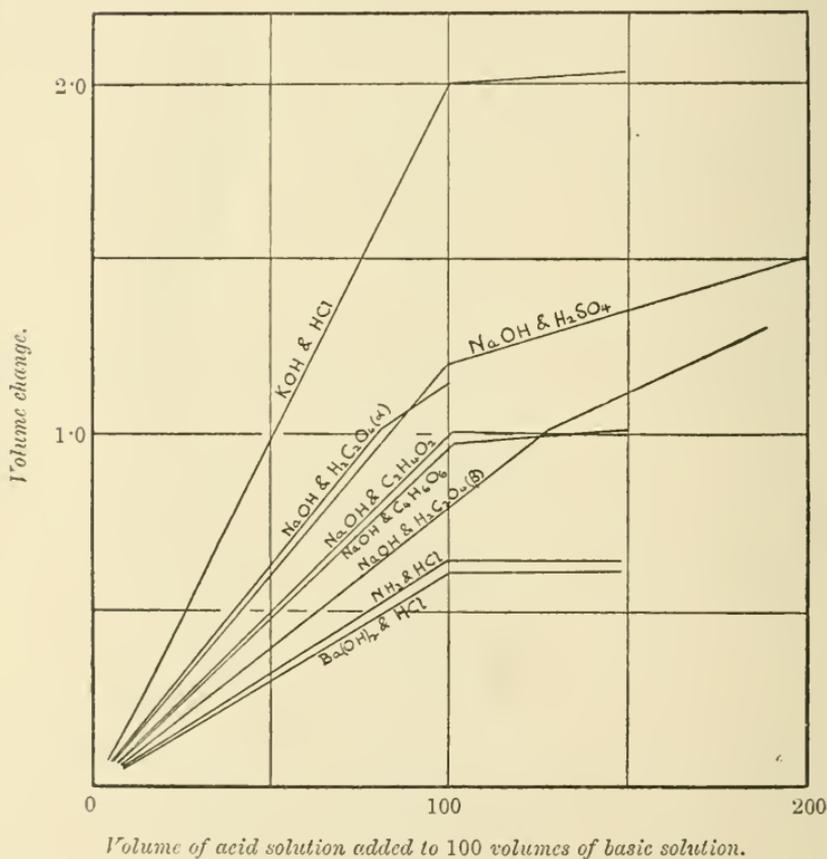
(vii) *Mixtures of Aqueous Sodium Hydroxide and Oxalic Acid*
(continued).

(8.) Density of oxalic acid solution = 1.01756.

Equivalent volumes 100NaOH aq. : 125H₂C₂O₄ aq.

Volume of sodium hydroxide solution.	Volume of oxalic acid solution.	Increase in volume after mixing.
100	21.34	+0.160
100	42.01	0.324
100	83.89	0.667
100	126.57	1.014
100	189.69	1.307

FIG. 1.



From the graphical representation of these results (Fig. 1) it is evident that the change in volume produced on neutralising a base with an acid is directly proportional to the quantity of salt formed. The view that this increase or decrease in volume is conditioned

by the solution volume of the salt is supported by the fact that, within wide limits, the volume change is independent of concentration. For instance, in the case of mixtures of *N*-sodium hydroxide with oxalic acid solutions of different strengths, practically the same increase in volume is obtained in corresponding molecular mixtures in the two sets of experiments (see Fig. 1). The same applies to other mixtures, and might be deduced from the fact that the solution volume of salts in water changes but little with the concentration.

When excess of acid is present, the volume change depends on the nature of the acid. Secondary interactions occur, as we know, in mixtures of sulphuric acid and oxalic acid with their salts in aqueous solution, and these are represented by curves differing in slope beyond the point of neutralisation according to the degree of physical change. When no physical interaction takes place between the acid and its salts, the change in volume beyond the point of neutralisation must be represented by a line parallel to the base line. This is exemplified in aqueous mixtures of bases with hydrochloric acid, and we should expect that mixtures of hydrochloric acid with its salts would, under these conditions, give no volume change.

The following mixtures were made in order to verify this conclusion :

Mixtures of Sodium Chloride and Hydrochloric Acid in Aqueous Solution.

Density of hydrochloric acid solution = 1.09372.
 (a.) ,, sodium chloride ,, = 1.13192.

Equimolecular volumes (gaseous) 100NaCl aq. : 60.4HCl aq.

Volume of hydrochloric acid solution mixed with 100 volumes of sodium chloride solution.	Change in volume.
7.69	+ 0.02
14.93	+ 0.01
20.18	0.00
30.36	0.00
60.70	- 0.01
121.43	- 0.02

(β.) Density of sodium chloride solution = 1.06874.

Equimolecular volumes (gaseous) 100NaCl aq. : 30.7HCl aq.

5.26	0.00
10.12	0.00
15.43	0.00
30.72	- 0.01
61.53	- 0.02

It is difficult to see how these simple facts of solution are to be explained on the assumption of hydrate formation or ionic dis-

sociation, or, since the volume change at any degree of dilution is dependent on the solution volume of the salt formed, by any theory not acknowledging the individuality of the liquid molecule under normal conditions.

Molecular Complexity in the Liquid State.

In order to form a conception of the equilibrium existing between two liquids mutually miscible without change in their chemical nature, we may assume the molecules to be severally represented by spheres of different degrees of electrification. If volume changes were conditioned only by the resultant of the quasi-electrical forces inherent in the molecules—acting at a distance—the maximum deviation in volume from the theoretical, when the number of molecules in a mixture remains constant, would occur when they are mixed together in equal proportions, and it would be possible to calculate the magnitude of the change for other mixtures from the expression:

$$\xi = a(100 - a)K,*$$

where “ ξ ” is the change in volume, and “ a ” the percentage of one set of molecules in the mixture. Attention has been drawn in previous communications to the influence of the weights and volumes of the interacting molecules on this normal change in volume at different concentrations, but if we consider only the cumulative effect of all physical forces when increasing quantities of one set of molecules are added to a fixed number of other molecules, it is evident that the resulting physical change, whatever its nature, must be capable of representation by an unbroken curve.

The curves shown in Fig. 2 represent the volumetric changes which occur on mixing water with sulphuric acid, methyl alcohol, and pyridine respectively, and are typical of those obtained in the case of aqueous mixtures of inorganic and organic liquids generally.

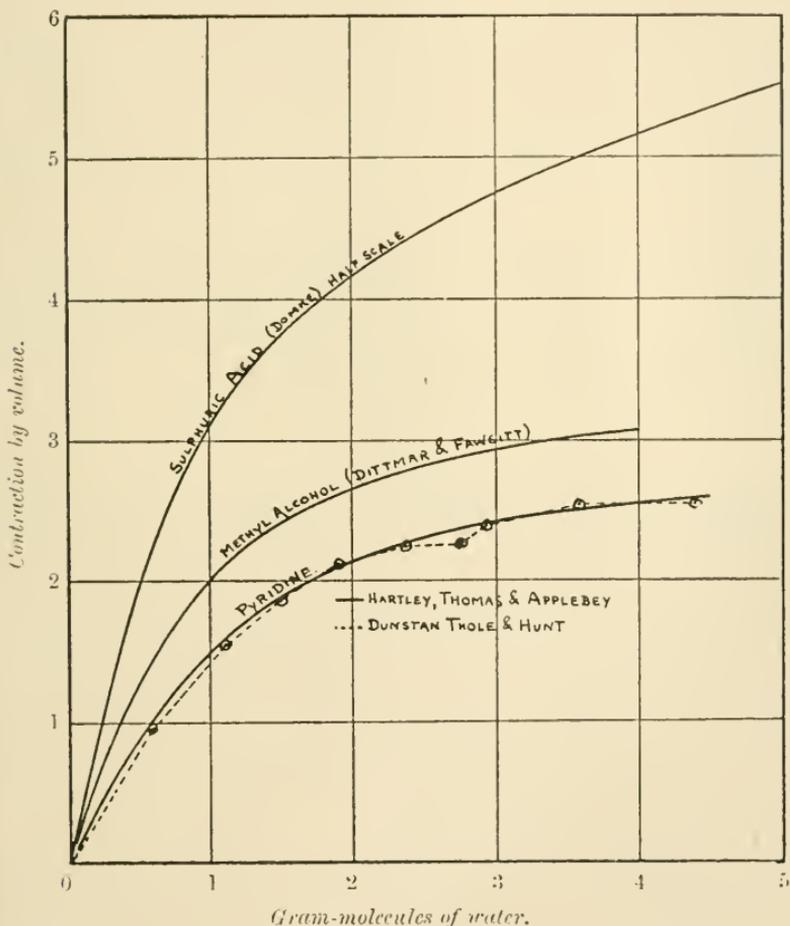
The base line represents gram-molecules of water mixed with one gram-molecule of each liquid (referred to the gaseous state) under constant conditions of temperature and pressure.

In arranging the material dealing with this subject, comparatively few cases have been noticed in which the physical changes interpreted as above fail to fall on smooth curves, and these have, on further investigation, been found to be due to experimental errors in the density determinations. Pyridine and water mixtures afford a case in point. Dunstan, Thole, and Hunt (Trans., 1907,

* For the application of this expression to aqueous mixtures, and to mixtures of sulphuric acid with its salts, see Trans., 1907, 91, 1606.

91, 1728), in the course of an investigation on the viscosity of mixtures of these liquids, drew attention to apparent discontinuities in the density curve, corresponding with similar discontinuities in the viscosity curve, and deduced the existence of certain hydrated complexes. More recently, Hartley, Thomas, and Applebey (Trans., 1908, 93, 538), while engaged on the same mixtures, point out discrepancies in the densities given by Dunstan,

FIG. 2.



Thole, and Hunt, and fail to verify the discontinuities in question. The pyridine-water curve in Fig. 2 represents the physical change deduced from Hartley, Thomas, and Applebey's figures, whilst the experimental points of Dunstan, Thole, and Hunt are also given.

The existence of such discontinuities would at once disprove the hypothesis on which we are attempting to explain these physical changes, and it is satisfactory to note that a repetition of the work

by Dunstan and Thole (Trans., 1908, **93**, 561) affords a contraction curve which is practically coincident with that of Hartley, Thomas, and Applebey.

An inspection of the above curves indicates that the rate of physical change rapidly diminishes when the proportion of water molecules (referred to the gaseous state) present in the mixture becomes greater than 50 per cent., and it was this circumstance which first suggested similar complexity in the case of these liquids, and by reason of the disturbing influences of mass and volume on the magnitude of the change in volume consequent on the existence of intermolecular spaces, subsequently led to the method of determining liquid complexities adopted by one of us in a previous communication (Holmes, Trans., 1906, **89**, 1780), and which depends on the apparent maximum change in the volume of the constituent of a mixture possessing the greater molecular volume.

If, however, we disregard for a moment the relative masses and volumes of the molecules in a mixture, and consider only the effect of physical forces acting at a distance, we obtain, by substituting different values for " ξ " in the expression :

$$\xi = \frac{\alpha\beta}{\alpha + \beta} K,^*$$

the following curves of volume change (Fig. 3) when increasing quantities (β) of one set of molecules are added to a fixed number (α) of the other molecules.

It is apparent that various means are at our disposal for the identification of an experimental curve as one of this order, and for fixing the point on the curve corresponding with a mixture of equal numbers of molecules. Perhaps the simplest is a graphical representation of the volume change plotted on a scale double that of the molecular concentration as indicated on the base line, when a tangential projection to the curve at this point will make an angle of 45° with the ordinate.

Many mixtures are known which afford curves approximating closely to this description, and those relating to aqueous mixtures of methyl alcohol, acetic acid, and pyridine are represented in Fig. 4.

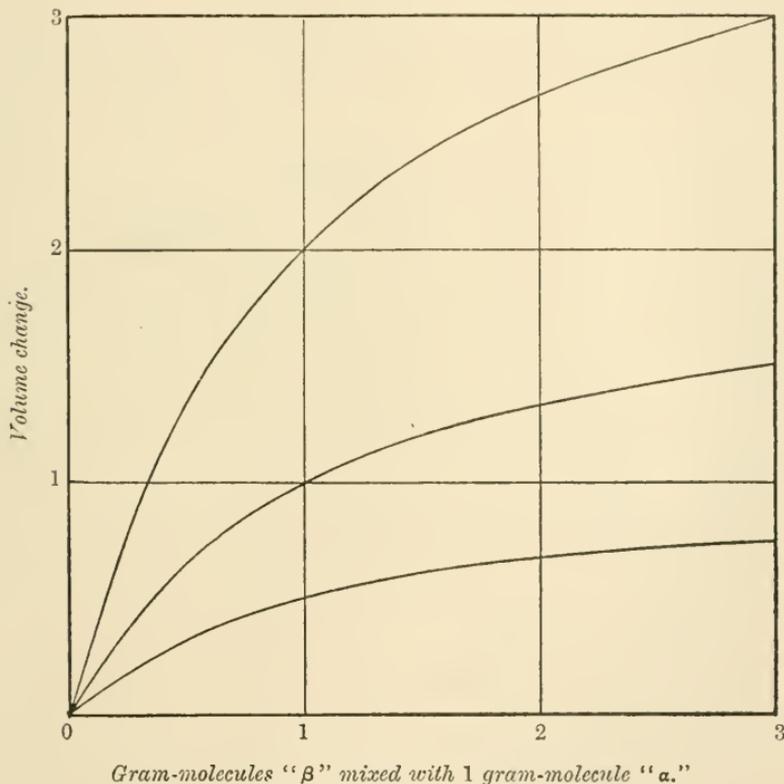
The corresponding curves yielded by other aqueous mixtures are very similar in character, and add weight to our previous deductions regarding the absence of hydrate formation in solution. The deviations from the theoretical physical curve we ascribe solely

* A modification of the expression $\xi = \alpha(100 - \alpha)K$, which represents the curve of volume change when the number of molecules in a mixture is constant.

to close-packing consequent on gravitational influences of mass on the intermolecular spaces, the extent of distortion being dependent on the relative volumes and masses of the molecules, and also on the magnitude of the change in volume.

In the absence of means of determining the values of these various constants in mixtures of liquids differing widely in their relative densities, and maybe in their molecular volumes, we have no alternative but to return to a consideration of the behaviour

FIG. 3.

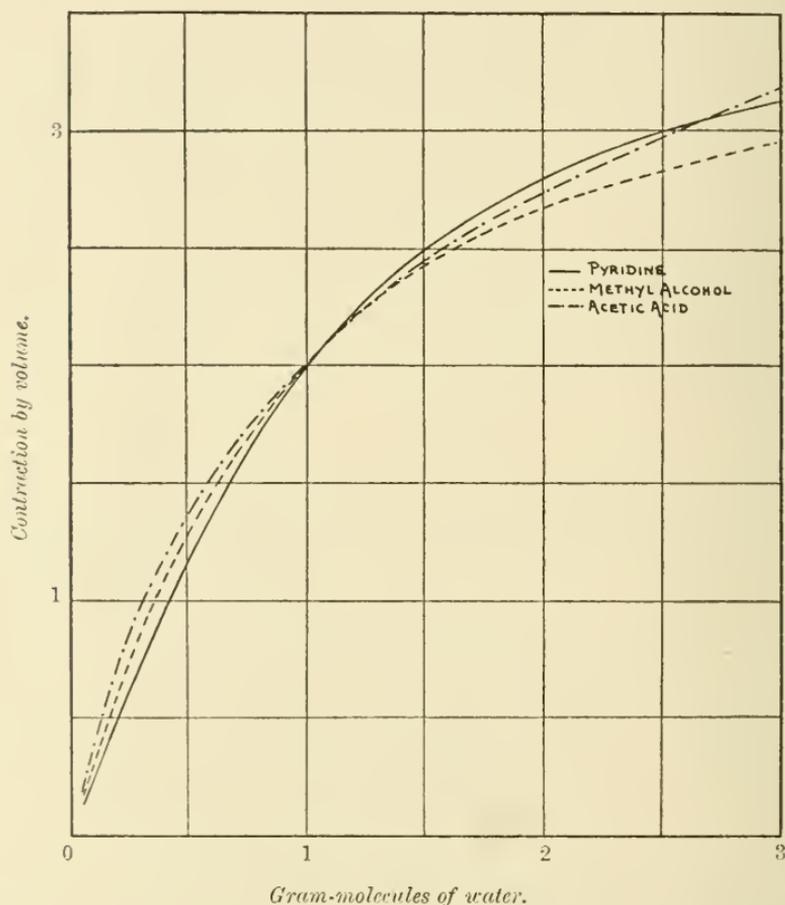


of a mixture of spheres of different radii as previously dealt with (Trans., 1906, 89, 1774).

If it be granted that the resultant of the forces inherent in the nature of the several molecules reaches a maximum at or near a mixture representing equal molecular proportions, it is evident that in this mixture the distance between the centres of mass of adjacent molecules will be either a maximum or a minimum, according to the nature of the volume change. Any method, therefore, which determines the quantities of the ingredients of a mixture necessary for this purpose will afford a means of ascer-

taining the relative complexities of liquid molecules. With a knowledge of the radii of the several molecular spheres, and since we are at liberty to assume that the volume change influences more in proportion the volume of the spheres of greater radii, it would appear that the necessary information will be given by the maximum difference between the initial and final proportions by

FIG. 4.



volume in a mixture of the constituent possessing the greater molecular volume.

Except, perhaps, in the case of homologous series, the question of deciding which molecule possesses the greater volume is open to doubt. A consideration of the data afforded by aqueous mixtures of the *n*-primary alcohols and aliphatic acids favours the view that the above method of interpretation is valid in these cases, and the application of the same principle to other than

aqueous mixtures gives strong support to the hypothesis that the intermiscibility of liquids is a function of the molecular volume (*loc. cit.*). This deduction, if correct, would go far in serving as a basis for a simple mechanical theory of solution, and the following series of mixtures were made with the view of obtaining further evidence in this direction.

Mixtures of Aniline with Methyl Alcohol.

In the generality of cases, miscibility in aqueous solution is accompanied by contraction in volume. There are many non-aqueous mixtures also known in which contraction occurs, and the following mixtures of aniline with methyl alcohol are representative of this class.

The form of pycnometer used for the determination of relative densities was a modification of that described by Linebarger (*Amer. J. Sci.*, 1896 [iv], 2, 226), one limb consisting of a capillary tube, whilst the terminals were fitted with capillary connexions and glass caps. The process of filling was conducted by means of a pressure pump, air being passed through a sulphuric acid washer into the weighing flask containing the liquid or mixture the density of which was required, thereby causing it to pass over and fill the pycnometer by way of the capillary limb. The pycnometer was then kept for one hour in a thermostat, the contents of which were agitated by a continuous stream of air-bubbles, and kept at 25° by means of a mercury-toluene regulator. The capacities of the pycnometers used in these experiments measured by their content of water at 25° were as follows:

	Grams of water.
A	25·0312
B	24·9861
C	25·0020

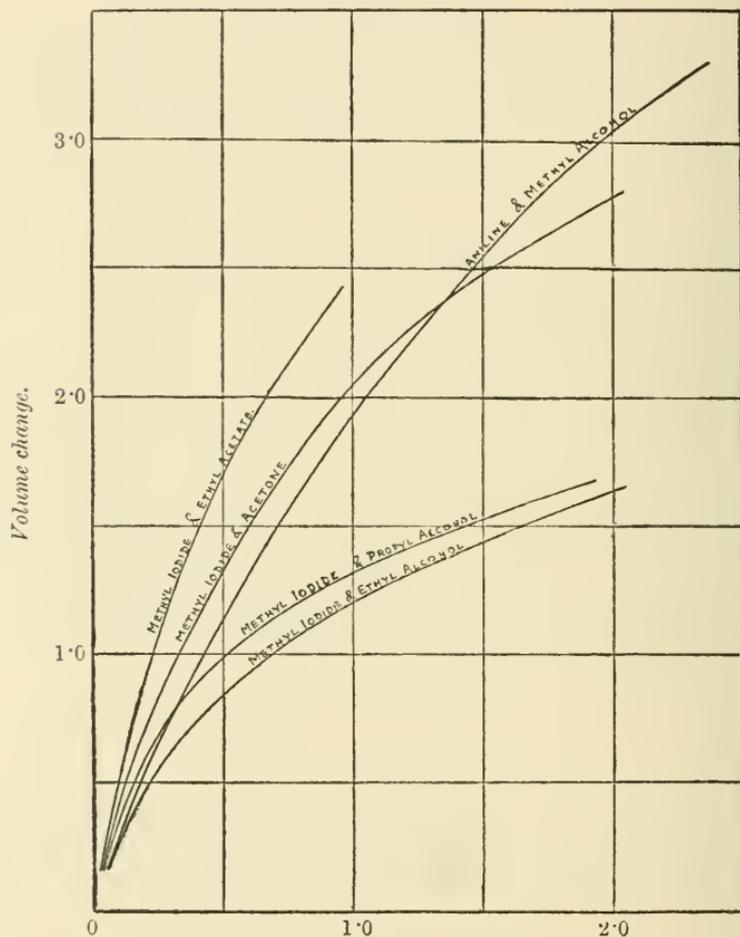
The boiling point of the sample of methyl alcohol (Kahlbaum's) was 64·8—65·0°, and its density at 25°/25° was 0·79042. The aniline had a boiling point of 184·0°, and a density at 25°/25° of 1·02060:

Weights in vacuum.		Density of mixture at 25°/25°.	When the volume of aniline is constant at 100 volumes.	
Aniline.	Methyl alcohol.		Relative volume of methyl alcohol.	Contraction in volume on mixing.
1.	2.	3.	4.	5.
(i) 26·2428	2·3961	1·00247	11·781	0·680
(ii) 24·1498	4·1488	0·98815	22·173	1·147
(iii) 22·0566	5·8567	0·97358	34·271	1·607
(iv) 20·3252	6·9369	0·96312	44·051	1·917
(v) 17·6773	8·9755	0·94391	65·533	2·509
(vi) 14·5323	11·8654	0·91740	105·377	3·302

Equimolecular volumes of the two liquids as given by the quotients of the molecular weights (referred to the gaseous state) by the relative densities at 25° are as 100 volumes aniline to 44.42 volumes methyl alcohol.

The curve in Fig. 5 represents the change in volume (column 5)

FIG. 5.



The base line represents molecular proportions (referred to the gaseous state) of methyl alcohol, ethyl alcohol, n-propyl alcohol, acetone, and ethyl acetate, mixed with 100 volumes of aniline and methyl iodide respectively.

when increasing quantities of methyl alcohol (column 4) are mixed with 100 volumes of aniline. By interpolating, the values were obtained for the volume change at different molecular mixtures, and from them were calculated the differences between the proportion of aniline (as the more insoluble and, according to the

above hypothesis, possessing therefore the greater molecular volume) in the initial and final volumes:

Molecular mixture (gaseous).		Contraction in volume when the volume of aniline is constant at 100 volumes.	Difference between the proportion of aniline in the initial and final volumes.
Aniline.	Methyl alcohol.		
1	0.25	0.65	0.530
1	0.50	1.15	0.778
1	0.75	1.57	0.894
1	1.00	1.93	0.938
1	1.25	2.25	0.944
1	1.50	2.53	0.925
1	1.75	2.77	0.891
1	2.00	2.99	0.852

It is evident that the greatest difference between the proportion of aniline in the initial and final volumes occurs at a mixture closely approximating to equal numbers of molecules referred to the gaseous state, thereby indicating that aniline possesses the same molecular complexity as methyl alcohol. Inferentially, therefore, aniline is similarly associated to water and the primary alcohols and aliphatic acids, and its molecular volume at 25°, as compared with water, is

$$\frac{93.096}{18.016} \times \frac{1}{1.0206} = 5.06.$$

As was noticed in the case of aqueous mixtures of the primary alcohols and aliphatic acids (*loc. cit.*), the point of maximum difference falls slightly beyond the mixture of equimolecular proportions, a circumstance already explained by close-packing due to differences in the radii of the molecular spheres of influence.

Mixtures of Methyl Iodide with Ethyl Alcohol, n-Propyl Alcohol, and Acetone.

In the case of non-aqueous mixtures, it often happens that a volume is obtained, after mixing, which is greater than the sum of the initial volumes of the constituents, and the following series of mixtures were made with the view of ascertaining how far the method we have adopted is applicable in these circumstances.

As a result of much preliminary work, it was found that the *n*-primary alcohols and acetone gave relatively large increases in volume when mixed with methyl iodide, and the opportunity was offered of comparing the results thus obtained with those furnished by the corresponding aqueous mixtures of these liquids.

The sample of methyl iodide was prepared from wood-naphtha, carefully purified, and fractionated. Its boiling point was 42.3–42.6°. The sample of ethyl alcohol was prepared by repeatedly treating rectified spirits of wine with powdered lime,

whilst the *n*-propyl alcohol and acetone were obtained from Kahlbaum.

The capacities of the three pycnometers, measured by their content of methyl iodide at 25°, were as follows:

	Grams of methyl iodide.
<i>A</i>	56·5109
<i>B</i>	56·4091
<i>C</i>	56·4413

The mean density of methyl iodide afforded by these figures is therefore 2·25760 at 25°/25°.

Mixtures of Methyl Iodide with Ethyl Alcohol.

Boiling point of ethyl alcohol = 78·38°.
Density at 25°/25° „ „ = 0·78892.

Equimolecular volumes (gaseous) 100CH₃I : 92·80C₂H₆O.

Weights in vacuum.		Density of mixture at 25°/25°.	When the volume of methyl iodide is constant at 100 volumes.	
Ethyl alcohol.	Methyl iodide.		Relative volume of ethyl alcohol.	Increase in volume.
(i) 1·1348	56·9203	2·17391	5·705	0·216
(ii) 2·3045	56·5247	2·09768	11·667	0·346
(iii) 4·2561	50·9563	1·96530	23·902	0·567
(iv) 7·2165	42·0453	1·76365	49·116	0·863
(v) 9·3124	35·1057	1·61374	75·910	1·100
(vi) 10·5956	31·0943	1·52302	97·512	1·232
(vii) 14·2311	21·3744	1·28708	190·528	1·662

Mixtures of Methyl Iodide with n-Propyl Alcohol.

Boiling point of *n*-propyl alcohol = 97·2—97·4°.
Density at 25°/25° „ „ = 0·80206.

Equimolecular volumes (gaseous) 100CH₃I : 119·06C₃H₈O.

Weights in vacuum.		Density of mixture at 25°/25°.	When the volume of methyl iodide is constant at 100 volumes.	
<i>n</i> -Propyl alcohol.	Methyl iodide.		Relative volume of <i>n</i> -propyl alcohol.	Increase in volume.
(i) 1·5417	58·4232	2·15183	7·428	0·257
(ii) 2·6795	54·5779	2·07387	13·819	0·386
(iii) 2·8880	56·1928	2·06649	14·466	0·398
(iv) 5·1682	48·4309	1·91127	30·037	0·689
(v) 8·3949	38·9151	1·69709	60·721	1·005
(vi) 10·4975	32·0286	1·54939	92·255	1·212
(vii) 12·0036	28·2780	1·45640	119·483	1·331
(viii) 15·4573	18·7997	1·23496	231·434	1·684

Mixtures of Methyl Iodide with Acetone.

Boiling point of acetone = $56.9-57.2^{\circ}$.
 Density at $25^{\circ}/25^{\circ}$,, = 0.78764 .

Equimolecular volumes (gaseous) $100\text{CH}_3\text{I} : 117.2\text{C}_2\text{H}_6\text{O}$.

Weights in vacuum.		Density of mixture at $25^{\circ}/25^{\circ}$.	When the volume of methyl iodide is constant at 100 volumes.	
Acetone.	Methyl iodide.		Relative volume of acetone.	Increase in volume.
(i) 1.5266	57.2418	2.15008	7.651	0.246
(ii) 2.7681	55.1398	2.06642	14.402	0.437
(iii) 4.9605	47.9377	1.91063	29.686	0.817
(iv) 8.1690	39.6197	1.69857	59.106	1.332
(v) 10.1997	32.2721	1.54552	90.670	1.743
(vi) 11.8551	27.9170	1.43775	121.826	2.077
(vii) 15.5123	18.4745	1.20943	240.884	2.824

The following values for the volume change at different molecular mixtures of these liquids with methyl iodide were determined from the graphical representation of the results (Fig. 5), and from them were calculated the differences between the proportion of methyl iodide in the initial and final volumes:

Molecular mixture (gaseous).	Expansion in volume when the volume of methyl iodide is constant at 100 volumes in its mixtures with:				Difference between the proportion of methyl iodide in the initial and final volumes of its mixtures with:			
	Ethyl alcohol, <i>n</i> -propyl acetone.	Ethyl alcohol.	<i>n</i> -Propyl alcohol.	Acetone.	Ethyl alcohol.	<i>n</i> -Propyl alcohol.	Acetone.	
Methyl iodide.	1	0.2	0.47	0.59	0.67	0.33	0.38	0.41
	1	0.4	0.73	0.88	1.14	0.39	0.40	0.52
	1	0.5	0.84	1.02	1.33	0.39	0.40	0.52
	1	0.6	0.93	1.09	1.49	0.38	0.37	0.51
	1	0.8	1.08	1.23	1.79	0.35	0.32	0.47
	1	1.0	1.21	1.33	2.03	0.32	0.28	0.43

From a consideration of these results, it is evident that the greatest difference between the proportion of methyl iodide by volume in the initial and final volumes occurs when the number of molecules of methyl iodide in the mixture is practically double that of each of the other liquids, indicating that acetone possesses the same molecular complexity as the *n*-primary alcohols—a result already deduced from the volume changes afforded by aqueous mixtures of these liquids—and that methyl iodide has twice this complexity.

The molecular volume of methyl iodide at 25° , compared with that of water at the same temperature, is therefore

$$\frac{141.994 \times 2}{2.2576 \times 18.016} = 6.98.$$

It will be noticed that in these cases where expansion in volume occurs, the close-packing of the molecules causes the point of maximum difference in the proportion of the liquid of greater molecular volume to be displaced slightly in the direction opposite to that observed when contraction takes place—a result which was to be expected.

Mixtures of Methyl Iodide with Ethyl Acetate.

Similar mixtures were made with methyl iodide and ethyl acetate, the results of which are as follows :

Boiling point of ethyl acetate = $77.0-77.3^{\circ}$.
Density at $25^{\circ}/25^{\circ}$ „ „ = 0.89350.

Equimolecular volumes (gaseous) $100\text{CH}_3\text{I} : 155.91\text{C}_2\text{H}_5\text{O}_2$.

Weights in vacuum.		Density of mixture at $25^{\circ}/25^{\circ}$.	When the volume of methyl iodide is constant at 100 volumes.	
Ethyl acetate.	Methyl iodide.		Relative volume of ethyl acetate.	Increase in volume.
(i) 2.3536	60.1754	2.11898	9.832	0.310
(ii) 4.4215	54.8778	2.00817	20.253	0.603
(iii) 7.0356	47.4884	1.86516	37.242	1.018
(iv) 9.3554	50.8072	1.74115	56.733	1.377
(v) 11.5193	37.0678	1.63724	78.118	1.698
(vi) 15.7150	26.4510	1.42218	149.346	2.412

These results, interpreted as above, indicate that ethyl acetate is similarly associated to water and the *n*-primary alcohols, and that its molecular volume in the liquid state at 25° , compared with water, is

$$\frac{88.064}{0.8935 \times 18.016} = 5.47.$$

In a previous communication, the property of solubility has been compared to the behaviour of a mixture of inelastic spheres of different radii. Liquids, for instance, having molecular volumes approximating closely to one another are miscible in all proportions, but when the distance between the centres of mass of molecules of either constituent becomes so great as to allow the smaller to pass through the interstitial spaces of the larger spheres, mutual miscibility ceases, and the greater this factor, proportionately less miscible the liquids become.

We do not presume, however, that the solubility of liquids in water is a direct function of the molecular volume as determined by the quotient of the molecular weight by density. The volume so obtained comprises the true molecular volume defined by the sphere of activity of the atoms composing the molecule (and of which we know little), together with the outer envelope or molecular

co-volume created by the resultant of the quasi-electrical forces inherent in each atomic arrangement, and which allows of the diverse volume changes observed in mixtures of liquids. If relative solubility were directly proportional to the molecular volume so determined, it would presuppose that no change occurred in the volume of the interacting spheres after mixing. All experiments prove, however, that such changes do occur, even in the case of substances possessing only slight solubilities, so that the relation of the molecular spheres to each other changes with the degree of physical change. When such volume changes are comparable in the case of partially miscible liquids possessing approximately the same molecular volume, a similar comparison is to be noticed in their solubility factors. Thus, ethyl acetate and ethyl ether yield considerable contractions in aqueous solution, and, having molecular volumes at 22° of 5.4 and 5.8 compared with that of water, are soluble in 100 volumes of water at this temperature to the extent of 9.26 volumes and 8.11 volumes respectively. Aniline, on the other hand, with a molecular volume of 5.1, gives little volume change with water, and, instead of possessing greater solubility by reason of its smaller initial volume, is soluble only to the extent of 3.48 volumes (Herz, *Ber.*, 1898, **31**, 2671, and Bancroft, *Phys. Rev.*, 1895, **3**, 131).

It is probable that this change in the relative radii of the several molecular spheres on mixing can be calculated within a near approximation, but as in most cases the volume change is small, the disturbing factor due to this circumstance is greatly minimised, and, inasmuch as the relative volumes occupied by liquid molecules must be represented by the quotient of the molecular weight in the gaseous state by density, or a simple multiple of this quantity (since it is inconceivable that the molecular weight should be less in the liquid than in the gaseous state), sufficient latitude is afforded for allowances of this nature.

There is great probability, therefore, that, just as vapour density determinations are indirectly of importance in fixing the molecular weights of gases, so a knowledge of density and solubility will also suffice for ascertaining relative complexity in the liquid state.

It has already been shown that this method is roughly applicable to carbon disulphide and other liquids the molecular volumes of which have previously been given (Trans., 1906, **89**, 1785), and although these volumes, through lack of available data, were compiled from densities at varying temperatures, the change is so slight within small ranges of temperature that they may be assumed to be sufficiently accurate for the purpose.

For example, if methyl iodide were similarly associated to water, its molecular volume at 25° would be

$$\frac{141.994}{2.2576 \times 18.016} = 3.49,$$

and it would be placed in the molecular volume table among the lower alcohols and fatty acids which are miscible with water in all proportions. If, however, we double the aggregation, the molecular volume becomes 6.98, which falls between the ascertained molecular volumes (at the same temperature) of *n*-amyl alcohol (6.04) and chloroform (8.93)—a position which agrees with the gradation in the solubility factors of these liquids in water (Rex, *Zeitsch. physikal. Chem.*, 1906, **55**, 355, and Herz, *loc. cit.*), and also with its molecular volume as ascertained above by volume change methods.

Heat Changes in Liquid Mixtures.

Just as we have reason to believe from the data at present at our disposal that the intermiscibility of liquids may be explained by a theory requiring the individuality of the molecules under normal conditions and a knowledge of their relative volumes, so it should be possible to explain other physical properties appertaining to liquid mixtures on the same hypothesis.

Miscibility of pure liquids with water not only results in a contraction in volume, but heat also is produced. It is customary to regard this evolution of heat as being analogous to the heat of neutralisation of acids and bases, and capable of explanation on the theory of hydrate formation. It is difficult, however, to reconcile the fact that, in most cases, the neutralisation of an acid by a base in aqueous solution results in a relatively large expansion in volume, whilst contraction usually accompanies the mixing of pure liquids with water. In the first instance, the heat evolved is undoubtedly due to chemical action, as a result of which the initial molecules of a mixture are wholly disintegrated and a new set of molecules produced. In the second case, the heat evolved must be ascribed to friction between the several envelopes or spheres of influence of the molecules consequent on forces of attraction, which result in the diminution in volume. In cases where contraction occurs we are obviously unable to draw deductions regarding the molecular condition of liquids from the mixture which yields a maximum of heat production, since the close-packing of molecules due to gravitational influences of mass on the interspaces must also cause friction and evolution of heat. For instance, when increasing quantities of water are added to a fixed volume of ethyl alcohol, although the rate of change of

heat production may be a maximum near the mixture of equal proportions of molecules, careful experiments show that the greatest evolution of heat occurs at a mixture approximating to the proportions $C_2H_6O, 8H_2O$.

Again, mixtures of liquids are known in which heat is absorbed, and we find in the generality of these cases that expansion in volume results.

In another class of mixtures, of which those of chloroform and ethyl alcohol are a type, heat is evolved in some mixtures and absorbed in others, and although few data are here available except those afforded by the work of Bussy and Buignet (*loc. cit.*), these are undoubtedly instances of the gravitational influences of mass on the interspaces causing a frictional evolution of heat, which is greater in magnitude at some concentrations than the heat absorbed as a result of the normal forces of repulsion inherent to the molecules, and which in many mixtures of these liquids results in an expansion in volume. Such peculiarities can only obtain in mixtures in which the normal change in volume is relatively small.

Few mixtures of liquids have hitherto been examined with the view of ascertaining the law of the change of temperature with concentration. The mixtures of methyl iodide with *n*-primary alcohols, yielding as they do relatively large expansions in volume, promised to afford valuable information in this direction.

In the following series of mixtures, the initial temperature of each constituent was adjusted to 15° , which temperature approximated closely to that of the room, and the change in temperature after mixing ascertained by means of a Schmidt and Haensch thermometer graduated to 0.1° . The volume of the mixture in each case was about 30 c.c.

Mixtures of Methyl Iodide with Methyl Alcohol.

Molecular mixture (gaseous).			Molecular mixture (gaseous).		
Methyl iodide.	Methyl alcohol.	Temperature change.	Methyl iodide.	Methyl alcohol.	Temperature change.
1	0.076	-4.0°	1	0.761	-6.8°
1	0.120	5.3	1	1.071	6.4
1	0.253	6.0	1	2.002	5.6
1	0.524	6.9			

Mixtures of Methyl Iodide with Ethyl Alcohol.

Molecular mixture (gaseous).			Molecular mixture (gaseous).		
Methyl iodide.	Ethyl alcohol.	Temperature change.	Methyl iodide.	Ethyl alcohol.	Temperature change.
1	0.061	-5.2°	1	0.818	-6.8°
1	0.126	6.0	1	1.051	6.4
1	0.258	7.0	1	2.053	5.6
1	0.529	7.3			

Mixtures of Methyl Iodide with n-Propyl Alcohol.

Molecular mixture (gaseous).			Molecular mixture (gaseous).		
Methyl iodide.	n-Propyl alcohol.	Temperature change.	Methyl iodide.	n-Propyl alcohol.	Temperature change.
1	0.062	-5.4°	1	0.510	-8.0°
1	0.116	6.2	1	0.775	7.8
1	0.122	6.3	1	1.004	6.9
1	0.252	7.5	1	1.944	5.1

Mixtures of Methyl Iodide with n-Amyl Alcohol.

Molecular mixture (gaseous).			Molecular mixture (gaseous).		
Methyl iodide.	n-Amyl alcohol.	Temperature change.	Methyl iodide.	n-Amyl alcohol.	Temperature change.
1	0.121	-6.5°	1	0.943	-6.9°
1	0.239	7.8	1	1.975	4.5
1	0.493	8.1			

In each series the maximum fall in temperature occurs at an admixture corresponding to two molecules of methyl iodide with one molecule of each alcohol (referred to the gaseous state), a result which confirms the complexities of these alcohols compared with methyl iodide as deduced above from volume change experiments.

The results of this investigation lend support to our previous deductions that physical forces only are operative in solution, and that theories requiring electrolytic dissociation, or combination of solvent with solute, are unnecessary for understanding many of the phenomena common to aqueous and non-aqueous mixtures. We adhere to the view that the properties of both mixtures of liquids and solutions are consistent with the entity of the liquid molecule, and we venture to think that we have made out a *prima facie* case for an electrical theory requiring only a knowledge of liquid complexities for the elucidation of the simple facts associated

with the property of solution. Much experimental work is necessary before such a theory could be regarded as established, but we would suggest it at least as a working hypothesis for further investigations in this field of research.

In conclusion, we desire to express our indebtedness to Sir Edward Thorpe, C.B., F.R.S., for facilities afforded us in carrying on this investigation.

THE GOVERNMENT LABORATORY,
LONDON.

CCXIV.—*Studies in Phototropy and Thermotropy.*
Part I. Arylidene- and Naphthylidene-amines.

By ALFRED SENIER and FREDERICK GEORGE SHEPHEARD.

IN a recent paper we described a series of Schiff's bases, salicylidene-amines, one of which, salicylidene-*m*-toluidine, was found to be highly phototropic (this vol., 441). Under the influence of light waves of high refrangibility, this compound was found to change from pale yellow to orange, and when removed from that influence to return to its original colour. The phenomenon was ascribed to reversible isomeric change. We have continued this inquiry, and now submit an account of further work, in which we have studied a number of other salicylideneamines and related compounds.

Including salicylidene-*m*-toluidine, we have now found five compounds which exhibit phototropy. Looking at the constitution of these, there does not appear to be any necessary relation between the nature or the position of the substituents and the phototropic property. They are all salicylidene derivatives, but many such derivatives are not phototropic, as is the case also with the analogous *o*-hydroxynaphthylidene compounds which we have examined. It may be noted that the phototropic property is destroyed by the substitution of methoxyl for hydroxyl; further, in the case of salicylidene-*m*-toluidine, by the substitution of hydroxyl or chlorine for the methyl group, and, in salicylidene-*p*-aminobenzoic acid, either by the substitution of chlorine or methyl for the carboxyl group or by the conversion of the acid into a metallic salt.

Early in this investigation it was observed that many of the coloured bases became deeper in colour on heating, and that this change, like phototropy, was reversible. The whole of the com-

pounds in hand were then subjected to an examination to obtain further evidence, if possible, of this property. Their colour changes were noted (1) between the ordinary temperature and the temperature just below their melting points, called "the higher temperature," and (2) between the ordinary temperature and the lowest temperature we could conveniently command, that of solid carbon dioxide, called "the lower temperature." This led to the interesting fact that most of the compounds exhibit this phenomenon. Among inorganic substances this property has long been known, we need only mention that at the temperature of solid carbon dioxide, sulphur becomes almost colourless, red mercuric oxide becomes yellow, and vermilion becomes scarlet, or, on heating, zinc oxide becomes yellow, and that all these return to the original colour at the ordinary temperature. This reversible change of colour in solids depending on the temperature we propose to call *thermotropy*.

In the case of the Schiff's bases, the change of colour with rise of temperature is from yellow to orange to red, and on lowering of temperature from red to orange to yellow, but in some cases at the low temperature the colour disappears altogether. The elucidation of this question, however, must await spectroscopic measurements.

The extreme instability of the Schiff's bases, particularly those derived from hydroxyaldehydes, their characteristic tendency to form isomerides, is further illustrated by the differently coloured modifications which can be obtained at will by varying the method of their preparation or the temperature of crystallisation. (For other instances of the changeability of Schiff's bases, see Anselmino, *Ber.*, 1905, **38**, 3989; 1907, **40**, 3465; also Manchot and Furlong, *Ber.*, 1909, **42**, 3030.) In this connexion, allusion may also be made to the changes which these bases undergo under the influence of different solvents indicated by the different shades of colour that they exhibit in solution.

Evidence is accumulating of reversible isomeric reactions, like those described in this paper, which are indicated by physical differences, such as changes of colour. It is possible that these may be explained by hypotheses, similar to that of Hantzsch and Werner, assuming intramolecular rearrangement; but in the case of phototropy and thermotropy it should not be forgotten that the substances exhibiting these phenomena are solids. No one will doubt, however, that these differences of colour depend on isomeric change of some kind; but in the case of solids we know practically nothing of their molecules, not even of their relative molecular weights. The molecules of solids are probably far more

complex than those of liquids or gases; indeed, they may be rather complex groups or aggregates of ordinary gaseous molecules, which would give rise to far more numerous possibilities of isomerism. It appears to us that phototropic and thermotropic reactions are more probably due to isomeric changes affecting the aggregation of molecules in solids than to intramolecular change of molecules derived from a study of gases.

The following compounds were obtained by the condensation of the respective aldehydes and amines, in the usual manner; generally in alcoholic solution, and without the application of heat.

Salicylidene-m-toluidine, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{C}_6\text{H}_4\text{Me}$.—This phototropic compound, which was described in a previous paper (*loc. cit.*), is thermotropic, and also exhibits differences of colour in solution in different solvents. No thermotropy could be observed at "the higher temperature," just below its melting point, the latter being so near the ordinary temperature, but at "the lower temperature," that of solid carbon dioxide, the yellow phototrope became paler in colour and returned to the original colour at the ordinary temperature. The darker phototrope was not altered appreciably in colour by cooling. Solutions in ether, benzene, or light petroleum are rather lighter in colour than those in chloroform, alcohol, or glacial acetic acid.

Salicylidene-m-toluidine hydrochloride, $\text{C}_{14}\text{H}_{13}\text{ON}\cdot\text{HCl}$, was obtained as a yellow, amorphous precipitate by passing a current of dry hydrogen chloride into a solution of the base in dry ether. In presence of water, the salt hydrolyses readily. It is not phototropic, but in presence of light and moist air it decomposes. Thermotropy was detected at "the higher temperature" (150°) by a darkening in colour, the original colour returning at the ordinary temperature. There was no change of colour at "the lower temperature." It melts at 182° (corr.):

0.2214 gave 0.1274 AgCl. $\text{HCl} = 14.63$.

$\text{C}_{14}\text{H}_{14}\text{ONCl}$ requires $\text{HCl} = 14.72$ per cent.

Salicylidene-m-toluidine picrate, $\text{C}_{14}\text{H}_{13}\text{ON}\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$.—Equimolecular proportions of salicylidene-*m*-toluidine and picric acid were dissolved in hot alcohol and mixed. Small, bright yellow needles separated immediately. This compound does not appear to be phototropic or thermotropic. It melts at 179° (corr.):

0.2130 gave 22.3 c.c. N_2 (moist) at 13° and 772 mm. $\text{N} = 12.57$.

$\text{C}_{20}\text{H}_{16}\text{O}_8\text{N}_4$ requires $\text{N} = 12.74$ per cent.

o-Methoxybenzylidene-m-toluidine, prepared by the interaction of *o*-methoxybenzaldehyde and *m*-toluidine, is a liquid, and was not further examined.

Salicylidene-o-4-xylidene, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_3\text{Me}_2$, is photo-

tropic. It consists of light yellow needles, which change to an orange colour when exposed to sunlight, and resume their original colour in the dark. At "the higher temperature" (70°), the yellow phototrope exhibits thermotropy by darkening in colour and returning to the original colour at the ordinary temperature; at "the lower temperature," it becomes temporarily paler. The darker phototrope showed no thermotropy except that when kept for a short time at 70° it became paler in colour, and at the ordinary temperature appeared to be identical with the yellow phototrope. The base is soluble in the usual organic solvents, the solutions in alcohol, chloroform, or acetic acid being darker in colour than those in ether, benzene, or light petroleum. It melts at 76° (corr.):

0.2185 gave 12.2 c.c. N_2 (moist) at 14° and 746 mm. $N = 6.45$.

$C_{15}H_{15}ON$ requires $N = 6.22$ per cent.

o-Methoxybenzylidene-*o*-4-xylylidine, $OMe \cdot C_6H_4 \cdot CH:N \cdot C_6H_3Me_2$, was prepared by the interaction of *o*-methoxybenzaldehyde and *o*-4-xylylidine. No indication of phototropy or thermotropy could be detected. It crystallises from alcohol in pale yellow prisms, and is very soluble in the usual organic solvents; the solution in glacial acetic acid is yellow: in other solvents it is colourless, or only pale yellow. It melts, forming a yellow liquid, at 45° (corr.):

0.2751 gave 14.0 c.c. N_2 (moist) at 18° and 769 mm. $N = 5.95$.

$C_{16}H_{17}ON$ requires $N = 5.86$ per cent.

Salicylidene-m-5-xylylidine and *salicylidene*mesidine were prepared, but, proving to be liquids, were not further examined.

Salicylidene-o-chloroaniline, $OH \cdot C_6H_4 \cdot CH:N \cdot C_6H_4Cl$, separated from the alcoholic solution as an oil, which on keeping solidified to a mass of pale yellow crystals. It is phototropic; when exposed to sunlight it becomes orange, and the original colour returns in the dark. Both phototropes exhibit thermotropy; at "the higher temperature" the yellow phototrope darkens in colour, the original colour returning at the ordinary temperature; the orange phototrope at this temperature loses colour, and at the ordinary temperature appears to be identical with the yellow phototrope. At "the lower temperature," both yellow and orange isomerides become much paler in colour. *Salicylidene-o*-chloroaniline dissolves easily in the usual organic solvents; the solutions in alcohol, chloroform, or glacial acetic acid are deeper in colour than those in ether, benzene, or light petroleum. The base melts at $82-83^{\circ}$ (corr.):

0.2436 gave 12.3 c.c. N_2 (moist) at 14° and 769 mm. $N = 6.00$.

$C_{13}H_{10}ONCl$ requires $N = 6.05$ per cent.

o-Methoxybenzylidene-*o*-chloroaniline, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{N}\cdot\text{C}_6\text{H}_4\text{Cl}$, was prepared from *o*-methoxybenzaldehyde and *o*-chloroaniline in alcoholic solution, separating as a yellow oil, which soon solidified. After crystallisation from light petroleum, it was obtained as pale yellow prisms. Neither phototropy nor thermotropy was detected. It is very easily soluble in benzene, chloroform, ether, or glacial acetic acid, more sparingly so in alcohol or light petroleum. The solutions are colourless, with the exception of that in glacial acetic acid, which is yellow. The base melts at 69° (corr.):

0.2378 gave 11.8 c.c. N_2 (moist) at 15° and 767 mm. $\text{N}=5.87$.

$\text{C}_{14}\text{H}_{12}\text{ONCl}$ requires $\text{N}=5.71$ per cent.

Salicylidene-m-chloroaniline, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{N}\cdot\text{C}_6\text{H}_4\text{Cl}$, crystallises from alcohol or light petroleum in orange-yellow leaflets. This base is not phototropic, but exhibits thermotropy. At "the higher temperature" the solid darkens, and at "the lower temperature" becomes much paler; in either case it returns to the original shade at the ordinary temperature. It dissolves readily in the usual organic solvents, with the exception of light petroleum, in which it is less soluble; the solutions in alcohol, chloroform, or glacial acetic acid are deeper yellow than those in benzene, ether, or light petroleum. The yellow alcoholic solution becomes much paler, and the slightly yellow solution in light petroleum becomes colourless at the temperature of solid carbon dioxide. *Salicylidene-m*-chloroaniline melts at 95° (corr.):

0.2455 gave 12.6 c.c. N_2 (moist) at 14° and 773 mm. $\text{N}=6.14$.

$\text{C}_{13}\text{H}_{10}\text{ONCl}$ requires $\text{N}=6.05$ per cent.

Salicylidene-p-chloroaniline, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{N}\cdot\text{C}_6\text{H}_4\text{Cl}$, crystallises from alcohol or benzene in brilliant yellow needles. It is not phototropic. Thermotropy is indicated at "the higher temperature" by a distinct darkening in colour, and at "the lower temperature" by the colour becoming much paler, in both cases returning to the original shade at the ordinary temperature. It dissolves in the usual organic solvents; the solutions in benzene, light petroleum, or ether are colourless, whilst those in alcohol, chloroform, or acetic acid are yellow. At the temperature of solid carbon dioxide, the colour of an alcoholic solution becomes distinctly paler. *Salicylidene-p*-chloroaniline melts at $102\text{--}103^\circ$ (corr.):

0.2395 gave 12.3 c.c. N_2 (moist) at 14° and 769 mm. $\text{N}=6.11$.

$\text{C}_{13}\text{H}_{10}\text{ONCl}$ requires $\text{N}=6.05$ per cent.

Salicylidene-m-aminophenol, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, separates in orange crystals on the addition of salicylaldehyde to a solution of *m*-aminophenol in dilute acetic acid. On dissolving in hot

benzene, and adding an equal volume of light petroleum, reddish-orange scales of the base are obtained. This compound is not phototropic, but exhibits thermotropy, the colour of the crystals becoming darker at "the higher temperature" and much paler at "the lower temperature," returning to the original colour in both cases at the ordinary temperature. It is easily soluble in alcohol, chloroform, or glacial acetic acid, forming deep yellow solutions; in ether, forming a pale yellow solution; in benzene or light petroleum, in both of which it is less soluble, the solutions are colourless. The deep yellow alcoholic solution becomes much paler at the temperature of solid carbon dioxide. Salicylidene-*m*-aminophenol melts at 128—129° (corr.):

0.2653 gave 14.9 c.c. N₂ (moist) at 15° and 766 mm. N = 6.63.

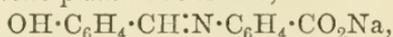
C₁₃H₁₁O₂N requires N = 6.57 per cent.

Salicylidene-p-aminobenzoic acid, OH·C₆H₄·CH:N·C₆H₄·CO₂H, crystallises from alcohol in bright yellow, silky needles. This compound is phototropic. When exposed to the action of sunlight, it darkens in colour, and returns to the original colour in the dark or in subdued daylight. Both the light and the dark coloured phototropes exhibit thermotropy. At "the higher temperature" both isomerides darken in colour; on cooling to the ordinary temperature, the paler phototrope resumes its original colour, and the same colour is exhibited by the deeper coloured phototrope, which apparently changes to the paler isomeride; at "the lower temperature" both phototropes become paler in colour. This base is easily soluble in alcohol, chloroform, or glacial acetic acid, less so in ether, benzene, or light petroleum. The solutions show about the same tint of yellow; the addition of water to the solution in glacial acetic acid, or of hydrogen chloride to the solution in alcohol, removes the colour, doubtless by hydrolysis. Salicylidene-*p*-aminobenzoic acid melts at 265—266° (corr.):

0.2134 gave 10.5 c.c. N₂ (moist) at 18.5° and 770 mm. N = 5.78.

C₁₄H₁₁O₃N requires N = 5.81 per cent.

Sodium salicylidene-p-aminobenzoate,



was prepared by dissolving *p*-aminobenzoic acid in hot alcohol, exactly neutralising with sodium hydroxide solution, and adding the calculated quantity of salicylaldehyde. Yellow prisms were obtained, very much paler in colour than the free acid. This salt is thermotropic, but not phototropic. At "the higher temperature" it changes to red, and at "the lower temperature" becomes almost colourless; in each case returning to its original tint at the ordinary temperature. It dissolves in cold water or alcohol, forming a deep yellow solution, which hydrolyses on warming:

0.7399 gave 0.1998 Na_2SO_4 . $\text{Na}=8.76$.

$\text{C}_{14}\text{H}_{10}\text{O}_3\text{NNa}$ requires $\text{Na}=8.68$ per cent.

Calcium salicylidene-p-aminobenzoate,

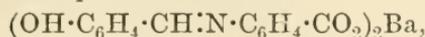


was obtained in pale yellow leaflets by the interaction of salicylaldehyde and an alcoholic solution of *p*-aminobenzoic acid, which was previously neutralised by calcium hydroxide solution. No phototropy could be detected, but thermotropy was observed by a darkening of colour at "the higher temperature." The salt dissolves in cold water, and the solution hydrolyses on warming:

0.6690 gave 0.1683 CaSO_4 . $\text{C}=7.41$.

$\text{C}_{28}\text{H}_{20}\text{O}_6\text{N}_2\text{Ca}$ requires $\text{C}=7.71$ per cent.

Barium salicylidene-p-aminobenzoate,



consists of small, yellow needles, and exhibits similar properties to the calcium salt. It is thermotropic, but not phototropic. At "the higher temperature" it becomes darker, and at "the lower temperature" paler in colour, the original colour returning, in each case, at the ordinary temperature.

For analysis, the salt was dried at 100° :

0.5551 gave 0.2110 BaSO_4 . $\text{Ba}=22.38$.

$\text{C}_{28}\text{H}_{20}\text{O}_6\text{N}_2\text{Ba}$ requires $\text{Ba}=22.25$ per cent.

o-Methoxybenzylidene-p-aminobenzoic acid,



was prepared in alcoholic solution, using *p*-aminobenzoic acid and *o*-methoxybenzaldehyde. It immediately separates in pale yellow needles, which, recrystallised from benzene, become much paler in colour. It is slightly thermotropic, but gives no indication of phototropy. It dissolves in alcohol, ether, or glacial acetic acid, and is sparingly soluble in benzene, chloroform, or light petroleum. The solutions are colourless, with the exception of that in acetic acid, which is yellow. The ether melts at 225.5° (corr.):

0.2469 gave 12.2 c.c. N_2 (moist) at 21° and 759 mm. $\text{N}=5.62$.

$\text{C}_{15}\text{H}_{13}\text{O}_3\text{N}$ requires $\text{N}=5.49$ per cent.

Salicylidene- α -naphthylamine, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{C}_{10}\text{H}_7$.—In a previous paper (*loc. cit.*) we described this compound as consisting of dark orange prisms which melt at 45.5° . We had overlooked an earlier description by Pope and Fleming (*Trans.*, 1908, **93**, 1916), who, however, obtained it in pale yellow needles melting at 53° . This shows the influence of slight alterations of the experimental conditions in determining the form of the product in the case of compounds containing the group $\cdot\text{CH}\cdot\text{N}\cdot$, which in so many

instances exhibit different properties in the hands of different observers (compare Hantzsch and Schwab, *Ber.*, 1901, **34**, 828). This compound is not acted on by light, but is thermotropic; at "the lower temperature" its dark orange colour changes to canary-yellow, the former colour returning at the ordinary temperature. Solutions of this base in ether, benzene, or light petroleum are paler in colour than those in other solvents. The colour of the alcoholic solution becomes temporarily paler at "the lower temperature."

Salicylidene-β-naphthylamine, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{C}_{10}\text{H}_7$. — This compound, previously prepared by Emmerich (*Annalen*, 1887, **241**, 351), exhibits marked phototropic and thermotropic properties, its colour showing reversible variations between yellow and orange or red. We are at present submitting this compound to a more detailed investigation. Emmerich gives the melting point of this compound as 121° ; the specimens we have prepared melt at 126° (corr.).

Disalicylidene-p-phenylenediamine, $(\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N})_2\text{C}_6\text{H}_4$, may be obtained either in pale yellow or orange-red plates. When the aldehyde and the diamine are brought together in alcoholic solution at a temperature below 50° , the mixture remains clear for a few minutes, and then the compound quickly separates in pale yellow plates. If, however, the temperature of the experiment be above 50° , a mixture of both isomerides is formed, the proportion of the red form increasing the higher the temperature employed, but contact of solvents, in such a proportion that only a small part dissolved with the yellow plates or the mixtures obtained, changes the yellow into the more stable red isomeride. The change of the yellow into the red form by this contact with solvents, accompanied, of course, with partial solution, takes place in a few minutes when the solvent is ethyl acetate, chloroform, benzene, or acetone; in half an hour to an hour when alcohol or ether is used; whilst with light petroleum several hours are requisite. It is noteworthy that the order of solvents just given corresponds with that of the solubility of the red isomeride; it is most soluble in the first group, and least soluble in light petroleum.

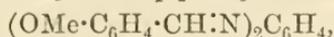
No phototropy could be detected in either isomeride, but both exhibit thermotropy, and, further, at 115° the yellow isomeride changes to the red. When the yellow isomeride is heated, it gradually deepens in colour, until, at about 110° , it becomes orange. If the temperature is then lowered, the reverse changes of colour take place; if, however, the temperature is allowed to rise above 110° , the orange colour changes gradually into red and deep red until the melting point is reached. On lowering the

temperature, the reverse changes of colour are observed until a temperature of about 115° is reached; below this temperature, the orange and yellow colour does not reappear, but the red merely becomes slightly paler. This isomeric change at 115° , not being reversible, is not phototropic, although it takes place under the thermotropic conditions pertaining to that temperature. At the temperature of solid carbon dioxide, the yellow isomeride gave no indication of thermotropy, but the red isomeride became yellow, returning to red at the ordinary temperature. The red isomeride melts at $212\text{--}213^{\circ}$ (corr.):

0.2192 gave 16.7 c.c. N_2 (moist) at 17° and 769 mm. $\text{N} = 8.94$.

$\text{C}_{20}\text{H}_{16}\text{O}_2\text{N}_2$ requires $\text{N} = 8.86$ per cent.

2: 2'-Dimethoxydibenzylidene-*p*-phenylenediamine,



was prepared by the interaction of the diamine and *o*-methoxybenzaldehyde in alcoholic solution. After recrystallisation from alcohol, pale yellow needles of the ether were obtained. It is not phototropic, and but slightly thermotropic. It dissolves readily in most organic solvents, sparingly in ether. In glacial acetic acid, the solution is dark red. The *hydrochloride*, which was prepared by passing hydrogen chloride into an ethereal or chloroformic solution of the base, is red, in the first instance, but soon changes to orange-yellow. The base melts at 152° (corr.):

0.2492 gave 17.7 c.c. N_2 (moist) at 17° and 766 mm. $\text{N} = 8.31$.

$\text{C}_{22}\text{H}_{20}\text{O}_2\text{N}_2$ requires $\text{N} = 8.14$ per cent.

m-Hydroxybenzylidene-*m*-toluidine, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH:N}\cdot\text{C}_6\text{H}_4\text{Me}$, was obtained in colourless crystals on the addition of the amine to the aldehyde solution. The crystals were dissolved in warm benzene, and light petroleum added, when long, colourless prisms of the base slowly separated. This compound is neither phototropic nor thermotropic. It dissolves readily in the usual organic solvents, but is sparingly soluble in light petroleum. With the exception of the solution in glacial acetic acid, which is yellow, the solutions are colourless. The *hydrochloride* is yellow. *m*-Hydroxybenzylidene-*m*-toluidine melts at $106\text{--}107^{\circ}$ (corr.):

0.2592 gave 14.6 c.c. N_2 (moist) at 16.5° and 765 mm. $\text{N} = 6.60$.

$\text{C}_{14}\text{H}_{13}\text{ON}$ requires $\text{N} = 6.64$ per cent.

p-Hydroxybenzylidene-*m*-toluidine, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH:N}\cdot\text{C}_6\text{H}_4\text{Me}$.—*m*-Toluidine was added to a solution of *p*-hydroxybenzaldehyde in hot benzene. Small, colourless crystals separated on cooling, which, dried in the air, became slightly yellow. When recrystallised from alcohol, pale yellow plates were obtained, whilst from benzene almost colourless crystals were obtained, the latter not very well defined.

Both the pale yellow crystals from alcohol and the almost colourless crystals from benzene, when rubbed in a mortar, became distinctly yellow. Whether these different colours represent or not distinct isomerides or isomeric mixtures was not determined.

This compound is not phototropic, but exhibits thermotropy. At "the higher temperature" the pale yellow crystals from alcohol deepen in colour, the original colour returning at the ordinary temperature; the colourless crystals from benzene do not change. At "the lower temperature" the yellow crystals become colourless, their colour returning at the ordinary temperature.

Both sets of crystals behave similarly towards solvents. The compound dissolves readily in alcohol, ether, glacial acetic acid, or ethyl acetate; less readily in chloroform or benzene; sparingly in light petroleum. The solutions are yellow except those in ether or benzene, which are almost colourless.

p-Hydroxybenzylidene-*m*-toluidine melts at 181° (corr.):

0.2663 gave 15.0 c.c. N₂ (moist) at 18° and 763 mm. N=6.53.

C₁₄H₁₃ON requires N=6.64 per cent.

Anisylidene-m-toluidine, OMe·C₆H₄·CH:N·C₆H₄Me, was prepared from anisaldehyde and *m*-toluidine. It crystallises from alcohol in small, colourless plates soluble in the usual organic solvents; in glacial acetic acid the solution is yellow; the other solvents give colourless solutions. It melts at 59° (corr.):

0.2922 gave 15.95 c.c. N₂ (moist) at 14.5° and 750 mm. N=6.32.

C₁₅H₁₅ON requires N=6.22 per cent.

Anisylidene-m-toluidine hydrochloride, C₁₅H₁₅ON, HCl.—A solution of the base in dry ether was saturated with dry hydrogen chloride, when the salt was precipitated as a pale yellow powder. It melts at 174° (corr.). When dissolved in alcohol and neutralised with a standard solution of sodium hydroxide, using phenolphthalein as indicator:

0.7553 required 27.4 c.c. (1 c.c.=0.003854 HCl). HCl=14.04.

C₁₅H₁₆ONCl requires HCl=13.93 per cent.

2-Hydroxy-5-methylbenzylidene-m-toluidine,



crystallises from alcohol in pale orange leaflets, very soluble in the usual organic solvents. It is not phototropic, but exhibits thermotropy; at "the higher temperature" it darkens in colour, and at "the lower temperature" it becomes paler, and returns to the original colour, in both cases, at the ordinary temperature.

In benzene, light petroleum, or ether, the solutions of this base

are faintly yellow, while those in acetic acid, alcohol, or chloroform are deep yellow; at "the lower temperature" the alcoholic solution exhibits thermotropy similar to the solid.

2-Hydroxy-5-methylbenzylidene-*m*-toluidine melts at 70° (corr.):

0.2672 gave 14.0 c.c. N₂ (moist) at 14° and 767 mm. N = 6.23.

C₁₅H₁₅ON requires N = 6.22 per cent.

2: 2'-Dihydroxy-5: 5'-dimethyldibenzylidene-*p*-phenylenediamine,
(OH·C₆H₃Me·CH:N)₂C₆H₄,

occurs apparently in two isomeric modifications; the one, crystallised from benzene, in bright yellow leaflets, which melt at 256° (corr.); the other, in yellowish-brown crystals, crystallised from glacial acetic acid, which melt about half a degree lower than the preceding isomeride. No indication of phototropy was observed, but both isomerides exhibit thermotropy at the "higher" and "lower temperatures." Both behave in the same manner towards solvents; in benzene, chloroform, or glacial acetic acid, they are sparingly soluble, and less soluble in alcohol or light petroleum:

0.2822 gave 20.1 c.c. N₂ (moist) at 18° and 760 mm. N = 8.23.

C₂₂H₂₀O₂N₂ requires N = 8.14 per cent.

5-Bromosalicylidene-*m*-toluidine, OH·C₆H₃Br·CH:N·C₆H₄Me, crystallises from alcohol in yellow plates mixed with slightly darker coloured prisms of a possible isomeride. No phototropy was detected, but thermotropy was observed at both "the higher" and "the lower temperatures." It dissolves easily in the usual organic solvents, the solutions in ether, benzene, or light petroleum being paler in colour than those in chloroform, alcohol, or glacial acetic acid. The base melts at 102—103° (corr.):

0.3262 gave 13.5 c.c. N₂ (moist) at 15° and 757 mm. N = 4.83.

C₁₄H₁₂ONBr requires N = 4.83 per cent.

5: 5'-Dibromodisalicylidene-*p*-phenylenediamine,
(OH·C₆H₃Br·CH:N)₂C₆H₄.

—This compound, after recrystallisation from nitrobenzene, was obtained in dark yellow leaflets almost insoluble in solvents of low boiling point. It is not phototropic, but exhibits thermotropy. At "the higher temperature" it is distinctly red, and at "the lower temperature" loses much of its yellow, in both cases returning to its original colour at the ordinary temperature. It melts at 306° (corr.):

0.2408 gave 12.2 c.c. N₂ (moist) at 18° and 767 mm. N = 5.91.

C₂₀H₁₄O₂N₂Br₂ requires N = 5.91 per cent.

3-Nitrosalicylidene-*m*-toluidine, OH·C₆H₃(NO₂)·CH:N·C₆H₄Me, was obtained from solution in alcohol in light red needles. It is

not phototropic, but exhibits thermotropy at both "the higher" and especially "the lower temperature." It dissolves readily in benzene, chloroform, or acetic acid, and is not so soluble in alcohol, ether, or light petroleum. The colour of the solutions is the same, but the solution in chloroform shows green fluorescence. Low temperature thermotropy was observed in the case of the alcoholic solution. It melts at 144—145° (corr.):

0.2309 gave 21.5 c.c. N₂ (moist) at 14° and 759 mm. N = 10.95.

C₁₄H₁₂O₃N₂ requires N = 10.94 per cent.

5-Nitrosalicylidene-m-toluidine, OH·C₆H₃(NO₂)·CH:N·C₆H₄Me, crystallises from alcohol in bright yellow needles. It is not affected by light, but exhibits thermotropy at both "the higher" and "the lower temperature." The behaviour towards solvents, including the fluorescence of the chloroformic solution, and the thermotropy of the alcoholic solution, is similar to that of the isomeride just described. It melts at 139° (corr.):

0.2113 gave 19.7 c.c. N₂ (moist) at 15° and 759 mm. N = 10.91.

C₁₄H₁₂O₃N₂ requires N = 10.94 per cent.

Vanillidene-m-toluidine, OH·C₆H₃(OMe)·CH:N·C₆H₄Me, crystallises from light petroleum in colourless, silky needles. It is not affected by light nor by temperatures below its melting point. It dissolves in the usual organic solvents; the solution in alcohol or acetic acid is deep yellow, in chloroform it is pale yellow, and in ether, benzene, or light petroleum, colourless. If the crystals are rubbed in a mortar, they become temporarily yellow. It melts at 96° (corr.), forming a yellow liquid:

0.2574 gave 13.2 c.c. N₂ (moist) at 16.5° and 751 mm. N = 5.90.

C₁₅H₁₅O₂N requires N = 5.81 per cent.

Piperonylidene-m-toluidine, CH₂:O₂:C₆H₃·CH:N·C₆H₄Me, crystallises from alcohol in small, colourless prisms. It is easily soluble in the usual organic solvents, giving colourless solutions, except the solution in glacial acetic acid, which is yellow. It melts at 71° (corr.):

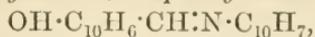
0.2964 gave 14.9 c.c. N₂ (moist) at 16° and 768 mm. N = 5.91.

C₁₅H₁₃O₂N requires N = 5.86 per cent.

2-Hydroxy-α-naphthylidene-m-toluidine, OH·C₁₀H₆·CH:N·C₆H₄Me, crystallises from alcoholic solution in orange-yellow needles. It is not affected by light, but shows thermotropy at both the "higher" and the "lower temperatures;" it dissolves in the usual organic solvents, exhibiting no differences of colour. It melts at 91.5° (corr.):

0.2376 gave 10.6 c.c. N₂ (moist) at 14° and 748 mm. N = 5.17.

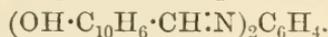
C₁₅H₁₅O₂N requires N = 5.37 per cent.

2-Hydroxy- α -naphthylidene- β -naphthylamine,

which has been previously described (Bartsch, *Ber.*, 1903, **36**, 1975), crystallises from alcohol in dark orange needles. It is not phototropic, but exhibits thermotropy at both "the higher" and "the lower temperatures." Its solutions show no difference of colour. Its hydrochloride is orange. We find, in agreement with Bartsch, that the base melts at 143° (corr.):

0.2242 gave 9.2 c.c. N₂ (moist) at 17.5° and 755 mm. N = 4.74.

C₂₁H₁₅ON requires N = 4.72 per cent.

2: 2'-Dihydroxy-di- α -naphthylidene-p-phenylenediamine,

—This compound consists of small, glistening, crimson-red crystals. It is sparingly soluble in organic solvents. It is not affected by light, but exhibits thermotropy both at "the higher" and "the lower temperatures." It melts at 307° (corr.):

0.2226 gave 13.1 c.c. N₂ (moist) at 18° and 760 mm. N = 6.80.

C₂₈H₂₀O₂N₂ requires N = 6.73 per cent.

Cinnamylidene-m-toluidine, C₆H₅·CH:CH·CH:N·C₆H₄Me, crystallises from alcohol in dark yellow prisms. It is neither phototropic nor thermotropic. It dissolves in the usual organic solvents, the solutions being yellow, except that in glacial acetic acid, which is red. It forms a deep yellow *hydrochloride*. The base melts at 124° (corr.):

0.2630 gave 14.4 c.c. N₂ (moist) at 17.5° and 759 mm. N = 6.33.

C₁₆H₁₅N requires N = 6.33 per cent.

UNIVERSITY COLLEGE,
GALWAY.

CCXV.—*The Condensation of Ketones and Aldehydes
with the Sodium Derivative of Ethyl Cyanoacetate.
Part II.*

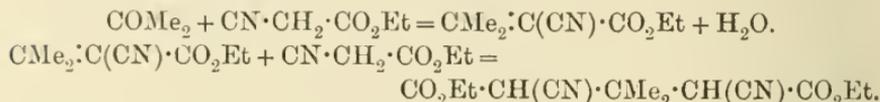
By HENRY DENT GARDNER, jun., and WALTER NORMAN HAWORTH.

In a previous communication by one of us (Haworth, this vol., 480), the condensation of cyclic ketones with ethyl sodiocyanoacetate, first studied by Harding, Haworth, and Perkin (*Trans.*, 1908, **93**, 1944), was extended to the more general cases of aldehydes and ketones, such as phenylacetaldehyde and acetophenone, in order to discover in

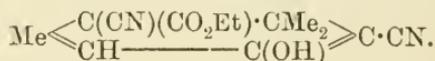
what direction this condensation might be useful for further synthetic work. The results which were obtained at that time seemed to make it desirable that simpler cases should be investigated, and the present communication is the outcome of experiments in this direction.

Komppa (*Ber.*, 1900, **33**, 3530) has studied the condensation of acetone with ethyl cyanoacetate, using a trace of piperidine as the condensing agent, and by a process which extended over many weeks he succeeded in isolating two definite products.

The reaction proceeded in two stages :

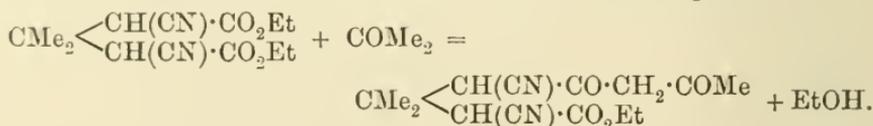


We have discovered that the condensation proceeds in quite an unexpected direction if sodium ethoxide is employed in the place of piperidine. When acetone is condensed with ethyl sodiocyanoacetate, the reaction is of a complicated character, the final product being *ethyl 2 : 6-dicyano-1 : 1 : 5-trimethyl- $\Delta^{2:4}$ -cyclohexadien-3-ol-6-carboxylate*,

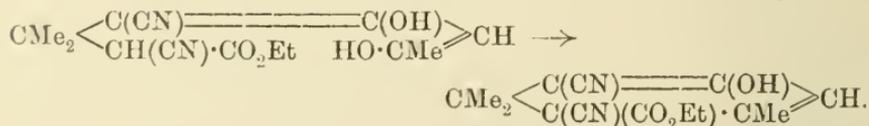


This substance, which melts at 135°, gives a green coloration in alcoholic solution with ferric chloride, and dissolves readily in sodium carbonate, the increased acidity being probably due to the close proximity of the cyano- to the hydroxy-group.

The course of the reaction may be expressed by assuming that the first product is ethyl $\alpha\alpha'$ -dicyano- $\beta\beta$ -dimethylglutarate, which was obtained as stated above by Komppa. The presence of sodium ethoxide in our experiments had the effect of inducing a secondary condensation with an extra molecule of acetone to take place :

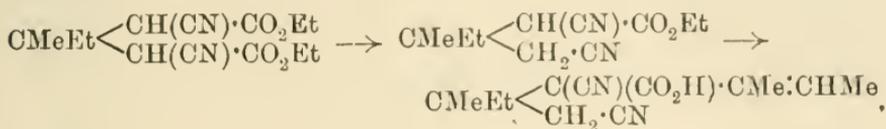


The latter substance contains four reactive hydrogen atoms, and in contact with hydrochloric acid undergoes tautomeric change, with the elimination of water and the formation of a six-membered ring :

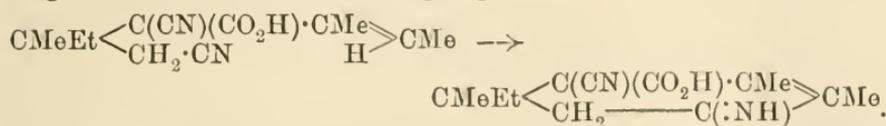


Striking confirmation of this view of the mechanism of the reaction was obtained from the condensation of ethyl cyanoacetate with methyl ketone. In this case the substitution of an ethyl group for one of the methyl groups in acetone, modified the result to some extent by

introducing the factor of steric hindrance, which was responsible for the loss of a carbethoxy-group in the form of ethyl carbonate. As before, the initial stage is evidently the formation of ethyl *aa'*-dicyano- β -methyl- β -ethylglutarate, which then reacts with another molecule of the ketone, hydrolysis taking place under the influence of sodium ethoxide :

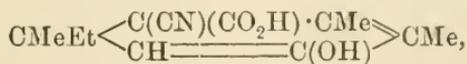


This open-chain compound subsequently condenses to a six-membered ring with formation of an imino-group :



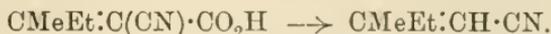
It is important to observe that this is another instance of the production of an alicyclic compound by the formation of the imino-grouping, which in the case of a five-membered ring has been so elegantly worked out by Dr. J. F. Thorpe (this vol., 685). We are indebted to his researches on the imino-compounds for the elucidation of the constitution of this and other compounds met with in this investigation.

The above imino-compound, 6-*imino-3-cyano-1 : 2 : 4-trimethyl-4-ethyl- Δ^1 -cyclohexene-3-carboxylic acid*, is yellow and melts at 108°. It dissolves readily in cold concentrated hydrochloric acid, and on digestion is converted into 3-*cyano-1 : 2 : 4-trimethyl-4-ethyl- $\Delta^{1:5}$ -cyclohexadien-6-ol-3-carboxylic acid*,



which is a liquid boiling at 193°/18 mm.

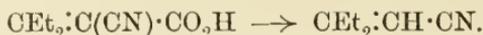
By a slight variation of the conditions, a simpler condensation product was subsequently obtained, namely, *a-cyano- β -methyl- β -ethylacrylic acid*, which on distillation is decomposed with elimination of carbon dioxide and formation of *β -methyl- β -ethylacrylonitrile* :



When this nitrile is hydrolysed under the conditions described in the experimental part of this paper (p. 1962), it yields *β -methyl- β -ethylacrylic acid*.

The constitution of the acid was controlled by oxidation with permanganate, when methyl ethyl ketone was recovered from the products and identified by its boiling point and the behaviour of its semicarbazone,

From a similar condensation of diethyl ketone with ethyl cyanoacetate, *α*-cyano-*β*-diethylacrylic acid was isolated, and this readily passes with loss of carbon dioxide into the corresponding *β*-diethylacrylonitrile:



The condensation has also been carried out with other homologues of acetone, namely, methyl propyl ketone and methyl hexyl ketone, with results which are exactly analogous to those described above; these are given in detail in the experimental part of this paper.

EXPERIMENTAL.

Ethyl 2:6-Dicyano-1:1:5-trimethyl-Δ^{2:4}-cyclohexadien-3-ol-6-



A good yield of this acid was obtained under the following conditions: Sodium (4.6 grams), dissolved in ethyl alcohol, was mixed with ethyl cyanoacetate (22.6 grams), and, after the separation of the white sodium derivative, acetone (11 grams) was added to the mixture. The white sodium derivative immediately dissolved, forming a clear yellow solution, which, on heating for an hour on the water-bath, deposited a yellow sodium salt. The product was cooled, dissolved in water, acidified with hydrochloric acid, and extracted with ether. The extract was washed several times with water, and afterwards with sodium carbonate, which dissolved the chief product of the reaction. This alkaline solution was acidified with excess of mineral acid, when an oil was deposited which, on keeping overnight, crystallised to a hard cake.

In another experiment, this oil was extracted with ether, and, after evaporation, was left to solidify in an open basin, but crystallisation did not take place even after the introduction of a crystal of the solid substance; it could only be induced to solidify by leaving it in contact with hydrochloric acid for several hours. The agency of hydrochloric acid is therefore necessary to complete the last stage of the synthesis. The substance was recrystallised from a mixture of benzene and light petroleum, or, better, from dilute methyl alcohol, from which it separates in colourless needles melting at 135°.

Owing probably to the strongly negative character of the hydroxy-group due to the proximity of a cyano-group, the compound dissolves readily in cold sodium carbonate, forming a deep yellow solution, which also decolorises permanganate instantly. It is readily soluble in benzene or alcohol, and in solution of the latter solvent it gives a deep green coloration with ferric chloride. It is sparingly soluble in water or light petroleum:

0.1220 gave 0.2880 CO₂ and 0.0680 H₂O. C = 64.4 ; H = 6.2.

0.1333 ,, 13.6 c.c. N₂ at 18° and 755 mm. N = 11.6.

C₁₄H₁₆O₃N₂ requires C = 64.6 ; H = 6.1 ; N = 10.8 per cent.

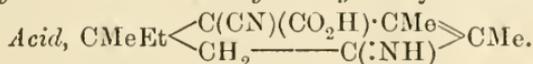
The *benzoyl* derivative crystallises from methyl alcohol in colourless needles, melting at 116°, and containing one molecule of water of crystallisation. This derivative dissolves in the ordinary organic solvents, but is insoluble in cold alkali, and gives no coloration with ferric chloride :

0.1123 gave 0.2700 CO₂ and 0.0600 H₂O. C = 65.6 ; H = 5.9.

0.1080 ,, 7.0 c.c. N₂ at 18° and 752 mm. N = 7.4.

C₂₁H₂₀O₄N₂·H₂O requires C = 66.0 ; H = 5.8 ; N = 7.3 per cent.

6-*Imino-3-cyano-1 : 2 : 4-trimethyl-4-ethyl-Δ¹-cyclohexene-3-carboxylic*



In preparing the above acid, sodium (11.5 grams), dissolved in absolute ethyl alcohol, was mixed with ethyl cyanoacetate (56.5 grams), and as soon as the white sodium compound had separated, methyl ethyl ketone (36 grams) was introduced into the very hot mixture, which was then heated for two hours on the water-bath. The white sodium compound first dissolved, forming a clear yellow solution, from which a bulky, yellow precipitate gradually separated. After cooling, the product was dissolved in water, acidified with very dilute hydrochloric acid, and extracted with ether. The ethereal solution was washed until free from alcohol and shaken with dilute sodium carbonate solution ; the slight residue remaining in the ether consisted of unchanged ketone and ethyl carbonate along with some neutral oils, the investigation of which is not yet complete. The sodium carbonate extract was acidified with dilute hydrochloric acid, the solution during the process being kept in violent agitation, until the oil suddenly became solid. This was immediately collected, well washed, and spread on porous porcelain, and, when quite dry, recrystallised from benzene, from which solvent it separated in light yellow needles, melting and decomposing at 108° :

0.1411 gave 0.3444 CO₂ and 0.0991 H₂O. C = 66.5 ; H = 7.8.

0.1516 ,, 16.6 c.c. N₂ at 12° and 762 mm. N = 13.0.

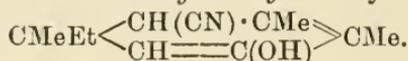
C₁₃H₁₈O₂N₂ requires C = 66.6 ; H = 7.7 ; N = 12.0 per cent.

A titration with *N*/10-sodium hydroxide gave the following results :

0.2698 required 0.0454 NaOH, whereas the same weight of a monobasic acid, C₁₃H₁₈O₂N₂, requires 0.0461 NaOH.

6-*Imino-3-cyano-1:2:4-trimethyl-4-ethyl- $\Delta^1:5$ -cyclohexene-3-carboxylic acid* is soluble in benzene or alcohol, but sparingly so in light petroleum; it decomposes slowly in contact with the air. Its solution in alcohol becomes deep brown on the addition of ferric chloride. It also dissolves at once in concentrated hydrochloric acid, which effects the hydrolysis of the imino-group.

3-*Cyano-1:2:4-trimethyl-4-ethyl- $\Delta^1:5$ -cyclohexadien-6-ol*,



The imino-compound just described was dissolved in cold concentrated hydrochloric acid, and, after twelve hours, the solution was diluted by adding twice its volume of water and digested for two hours in a reflux apparatus; carbon dioxide was evolved and an oily layer appeared on the top of the liquid. This was extracted with ether, evaporated, and distilled under diminished pressure, when almost the whole passed over at 193—194°/18 mm. as a colourless oil. The product was now insoluble in cold sodium carbonate, although it dissolved slightly on boiling; the oil dissolved at once in potassium hydroxide when sufficiently dilute, forming a yellow solution, but the potassium salt is only sparingly soluble in concentrated alkali:

0.1002 gave 0.2780 CO₂ and 0.0782 H₂O. C = 75.6; H = 8.7.

0.1136 „ 7.5 c.c. N₂ at 18° and 758 mm. N = 7.6.

C₁₂H₁₇ON requires C = 75.4; H = 8.9; N = 7.3 per cent.

The substance is an oil with an odour resembling that of a nitrile; its solution in alcohol gives a dark red coloration with ferric chloride. It readily forms a *benzoyl* derivative, but as this showed no signs of crystallising it was distilled under diminished pressure, when it boiled constantly at about 250°/40 mm., and gave the following numbers on analysis:

0.1177 gave 0.3307 CO₂ and 0.0749 H₂O. C = 76.7; H = 7.1.

C₁₉H₂₁O₂N requires C = 77.3; H = 7.1 per cent.

The *benzoyl* derivative is insoluble in alkalis, and does not give a coloration with ferric chloride.

The *carbonate* of the hydroxy-acid was also prepared by leading a stream of carbonyl chloride into an aqueous solution of the potassium salt. An oil was precipitated, which was extracted with ether, and, as it did not solidify, was distilled under 25 mm. pressure, when it passed over at 260° as a viscid, colourless liquid:

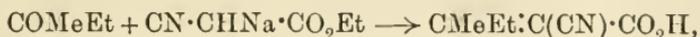
0.1203 gave 0.3228 CO₂ and 0.0866 H₂O. C = 73.2; H = 8.0.

C₅H₂₃O₃N₂ requires C = 73.5; H = 7.8 per cent.

β -Methyl- β -ethylacrylonitrile, CMeEt·CH·CN.

By a modification of the method employed in the condensation of equimolecular quantities of methyl ethyl ketone and ethyl sodiocyanoacetate described above (p. 1959), an oily mixture was obtained which could not be crystallised; it is explained below that this was due to the course of the initial reaction having proceeded in a rather different direction. In the former preparation care was taken to bring together the reacting substances in such a way as to produce as vigorous a reaction as possible at the beginning; but if on the other hand the reagents are allowed to cool before mixing, and the initial stage of the condensation is thus rendered less violent, the oil which is precipitated from the sodium carbonate solution by mineral acid does not crystallise.

Subsequent investigation showed that the course which the reaction follows under these conditions is:



whilst at the same time a small quantity of 6-imino-3-cyano-1:2:4-trimethyl-4-ethyl- Δ^1 -cyclohexene-3-carboxylic acid (p. 1959) is also formed. This was demonstrated by submitting the oily mixture of acids to fractional distillation under diminished pressure; the process is accompanied by the elimination of carbon dioxide and the formation of an oil possessing the disagreeable odour of a nitrile, which passed over at 95—105°/100 mm. in the first instance. A further small fraction was collected at 180°/150 mm. The lower boiling fraction consisted of β -methyl- β -ethylacrylonitrile, which was further purified by repeated distillation, and then analysed:

0·1308 gave 17·1 c.c. N₂ at 16° and 743 mm. N = 14·9.

C₆H₉N requires N = 14·7 per cent.

β -Methyl- β -ethylacrylonitrile is a colourless, mobile liquid, which distils at 101°/100 mm.

The higher boiling fraction gradually solidified, and, after draining on porous porcelain, was recrystallised from benzene, from which solvent it separates in long needles melting at 184°. The investigation of this substance is not yet complete; it seems to possess a high molecular weight and a rather complex constitution:

0·1789 gave 0·4647 CO₂ and 0·0929 H₂O. C = 70·8; H = 5·8.

0·1211 „ 16·6 c.c. N₂ at 16° and 756 mm. N = 15·9.

After the fractionation a considerable residue remained behind in the flask, which was found to have crystallised; this on purification melted at 108°, and was identified as the iminocarboxylic acid of this melting point.

β-Methyl-β-ethylacrylic Acid, CMeEt·CH·CO₂H.

The hydrolysis of β-methyl-β-ethylacrylonitrile is best carried out by digesting it for twenty-four hours with 20 per cent. alcoholic sulphuric acid, when, on cooling, crystals of ammonium sulphate separate out. The product was poured into water, extracted with ether, the ethereal solution well washed with water, and then evaporated. The residual oil was digested for a few minutes with methyl-alcoholic potash, then poured into water, and the neutral portion extracted with ether. The aqueous solution was acidified, when an oil separated, which was dissolved in ether, and the ethereal solution was dried and evaporated; the residue distilled at 208° under the ordinary pressure:

0.1143 gave 0.2640 CO₂ and 0.0900 H₂O. C = 63.0; H = 8.8.

C₆H₁₀O₂ requires C = 63.2; H = 8.8 per cent.

A titration with *N*/10-sodium hydroxide gave the following result: 0.2042 required 0.0720 NaOH, whereas the same weight of a monobasic acid, C₆H₁₀O₂, requires 0.0717 NaOH.

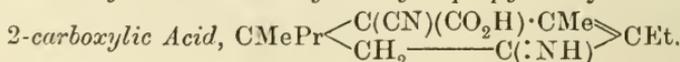
β-Methyl-β-ethylacrylic acid is a colourless, mobile liquid, possessing an odour characteristic of olefinic acids; it is sparingly soluble in water, and a solution of its sodium salt instantly decolorise permanganate.

The *anilide* is a colourless substance melting at 93—94°:

0.0800 gave 5.4 c.c. N₂ at 20° and 752 mm. N = 7.6.

C₁₂H₁₅ON requires N = 7.4 per cent.

Oxidation.—About 5 grams of the acid were dissolved in excess of dilute sodium carbonate in presence of powdered ice, and a 1 per cent. solution of potassium permanganate was slowly added. As soon as the oxidation was complete, the product was subjected to steam distillation, when an oil having the odour of a ketone passed over and was salted out from the distillate and extracted with ether. After removal of the ether, an oil, boiling at about 80°, remained, which was easily identified as methyl ethyl ketone by its general properties and by the melting point of its semicarbazone.

5-Imino-2-cyano-1 : 3-dimethyl-6-ethyl-3-propyl-Δ⁶-cyclohexene-

A hot solution of sodium (5.7 grams) in alcohol was treated with ethyl cyanoacetate (28 grams), and, after the separation of ethyl sodio-cyanoacetate, methyl propyl ketone (21.5 grams) was quickly added to the hot mixture. The reaction proceeded as before, and the product was worked up as described in the previous cases. The amount of

neutral oil formed was too small to investigate; the acid separated from the sodium carbonate extract as an oil, which, on stirring, soon solidified. It was collected, washed, drained on a porous tile, and then recrystallised from benzene, in which solvent it is almost insoluble in the cold; it separates in glistening leaflets, melting and decomposing at 113—114°:

0.1672 gave 0.4226 CO₂ and 0.1290 H₂O. C = 68.9; H = 8.6.

0.1504 ,, 13.7 c.c. N₂ at 13° and 746 mm. N = 10.6.

C₁₅H₂₂O₂N₂ requires C = 68.7; H = 8.4; N = 10.7 per cent.

A titration with *N*/10-sodium hydroxide gave the following results: 0.3160 required 0.0479 NaOH, whereas the same weight of a monobasic acid, C₁₅H₂₂O₂N₂, requires 0.0482 NaOH.

The imino-acid decomposes slowly on exposure to the air; it is readily soluble in alcohol or hot benzene, but only sparingly so in light petroleum. Concentrated hydrochloric acid dissolves it at once, effecting the hydrolysis of the imino-group and the production of the corresponding hydroxy-acid. The addition of ferric chloride to a little of the acid dissolved in alcohol causes the precipitation of a brown substance.

β-Methyl-β-propylacrylonitrile, CMePr·CH·CN.

By moderating the conditions of the experiment described above, so as to produce a less energetic reaction, an oily mixture of acids, similar in constitution to that obtained under parallel conditions in the case of methyl ethyl ketone (p. 1961), was precipitated from the sodium carbonate solution. The oil was dissolved in ether as before, and the oily residue, after evaporation, was slowly distilled under diminished pressure, when almost the whole passed over between 90° and 100°/30 mm. The initial product of the condensation is doubtless α-cyano-β-methyl-β-propylacrylic acid, which readily passes on distillation into *β*-methyl-β-propylacrylonitrile. This is a light, colourless oil, possessing the pungent odour characteristic of nitriles, and boiling at 95—96°/30 mm.:

0.1530 gave 17.4 c.c. N₂ at 12° and 748 mm. N = 13.2.

C₇H₁₁N requires N = 12.8 per cent.

β-Methyl-β-propylacrylic Acid, CMePr·CH·CO₂H.

The nitrile just described was readily hydrolysed by digesting it for eighteen hours with 20 per cent. alcoholic sulphuric acid, and subsequently treating the ester thus formed with methyl-alcoholic potash (see p. 1962). On acidifying the solution of the potassium salt, an oil was obtained which distilled at 222—225° under ordinary pressure. This acid is a mobile, colourless liquid, having the odour of fatty acid

a solution of its sodium salt decolorised permanganate instantly; it also combines freely with bromine in a chloroform solution:

0.1265 gave 0.3019 CO₂ and 0.1058 H₂O. C = 65.1; H = 9.3.
C₇H₁₂O₂ requires C = 65.6; H = 9.4 per cent.

β-Methyl-β-hexylacrylonitrile and β-Methyl-β-hexylacrylic Acid,
C₆H₁₃·CMe·CH·CO₂H.

Sodium (4.6 grams), dissolved in alcohol, was mixed with ethyl cyanoacetate (22.6 grams), and to the hot solution methyl hexyl ketone (26 grams) was added, and the product worked up as described in previous cases (p. 1959). In this example, no solid acid was isolated in the first instance, so that the oil was subjected to fractional distillation under 100 mm. pressure, when carbon dioxide was eliminated, and a large fraction of oil was collected at about 130°. A considerable residue remained behind in the flask, and a portion of this afterwards solidified (see below). The distillate was further purified, and, on analysis, gave numbers agreeing with the formula of *β-methyl-β-hexylacrylonitrile*:

0.1220 gave 9.8 c.c. N₂ at 15° and 762 mm. N = 9.4.
C₁₀H₁₇N requires N = 9.3 per cent.

This nitrile was digested for eighteen hours with 20 per cent. alcoholic sulphuric acid, and the resulting ester treated with methyl-alcoholic potash. On acidifying the alkaline solution after adding water, an oily acid was obtained which distilled constantly at 158°/20 mm. *β-Methyl-β-hexylacrylic acid* is a colourless oil, possessing an olefinic odour, and when dissolved in sodium carbonate it decolorises permanganate at once:

0.1560 gave 0.4030 CO₂ and 0.1502 H₂O. C = 70.4; H = 10.7.
C₁₀H₁₈O₂ requires C = 70.6; H = 10.6 per cent.

To determine its basicity, the acid was titrated with *N*/10-sodium hydroxide: 0.1860 required 0.0431 NaOH, whereas the same weight of a monobasic acid, C₁₀H₁₈O₂, requires 0.0435 NaOH.

5-Imino-2-cyano-1:3-dimethyl-6-amyl-3-hexyl-Δ⁶-cyclohexene-2-carboxylic Acid, C₆H₁₁·CMe < $\begin{array}{l} \text{C(CN)(CO}_2\text{H)·CMe} \\ \text{CH}_2 \text{-----C(:NH)} \end{array} \right> \text{C·C}_5\text{H}_9$.

It is mentioned above that the residue remaining in the flask after the distillation of the product obtained from the condensation of methyl hexyl ketone partly solidified, and this solid was found to be an acid. It was further purified by dissolving in sodium carbonate and reprecipitating with mineral acid, when a solid separated. This was collected and drained on porous porcelain, and then recrystallised from methyl alcohol, from which solvent it

separates in almost colourless leaflets, melting and decomposing at 136—137°. The analytical results indicate that it is an iminocyclohexenecarboxylic acid, analogous to those previously described on p. 1959, and, like these, it is unstable towards permanganate

0·1181 gave 0·3165 CO₂ and 0·1009 H₂O. C = 73·1 ; H = 9·5.

0·1172 „ 8·5 c.c. N₂ at 15° and 760 mm. N = 8·4.

C₂₁H₃₄O₂N₂ requires C = 72·8 ; H = 9·8 ; N = 8·1 per cent.

Hydrochloric acid effects the hydrolysis of the imino-group, forming the corresponding hydroxycarboxylic acid.

α-Cyano-ββ-diethylacrylic Acid, C₈H₁₁O₂N·C(CN)·CO₂H.

Ethyl sodiocyanoacetate was prepared by treating ethyl cyanoacetate (28 grams) with sodium (5·7 grams) dissolved in alcohol, adding diethyl ketone (21·5 grams) to the hot mixture, and boiling the whole for two hours on the water-bath. The reaction proceeded rather more slowly than in experiments with other ketones, and the yield of oil obtained from the sodium carbonate solution was much smaller. The product was worked up exactly as in other cases, and, after some days, the oily acid deposited large crystals, which were pressed on a porous tile and, when free from oil, recrystallised from light petroleum, from which the substance separated in colourless, elongated prisms melting at 55°. *α-Cyano-ββ-diethylacrylic acid* is sparingly soluble in light petroleum, very soluble in benzene, ethyl acetate, or alcohol.

A titration showed it to be monobasic: 0·1374 required 0·0360 NaOH, whereas the same weight of a monobasic acid, C₈H₁₁O₂N, requires 0·0359 NaOH.

0·1474 gave 0·3431 CO₂ and 0·0964 H₂O. C = 63·4 ; H = 7·2.

0·1448 „ 11·2 c.c. N₂ at 13° and 758 mm. N = 9·1.

C₈H₁₁O₂N requires C = 62·7 ; H = 7·2 ; N = 9·1 per cent.

The above cyano-acid is decomposed on distillation with elimination of carbon dioxide and formation of *ββ-diethylacrylonitrile*, which is a colourless oil distilling at 90°/25 mm. We were unable through lack of material to prepare the corresponding *ββ*-diethylacrylic acid by hydrolysis of the nitrile :

0·1644 gave 19·0 c.c. N₂ at 16° and 745 mm. N = 13·1.

C₇H₁₁N requires N = 12·8 per cent.

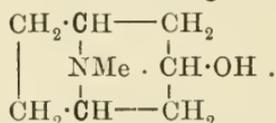
We desire to express our indebtedness to Prof. W. H. Perkin for the interest he has taken in this investigation.

THE UNIVERSITY,
MANCHESTER.

CCXVI.—*The Configuration of Tropine and ψ -Tropine, and the Resolution of Atropine.*

By MARMADUKE BARROWCLIFF and FRANK TUTIN.

THE base tropine, obtained by the hydrolysis of the alkaloids atropine and hyoscyamine, has been shown by Willstätter (*Ber.*, 1898, **31**, 1534) to possess the following constitutional formula:



Liebermann (*Ber.*, 1891, **24**, 2332) obtained from Java coca leaves an alkaloid, designated tropacocaine, which he proved to be the benzoyl derivative of a base isomeric with tropine. This base has been designated ψ -tropine, and Willstätter has shown (*Ber.*, 1896, **29**, 936) that it may readily be obtained from tropine by heating the latter with sodium amyloxyde.

Tropine and ψ -tropine both possess the same structural formula, for, on oxidation, they each yield tropinone, whilst the latter, when reduced, gives a mixture of the two hydroxy-bases (Willstätter and Iglauer, *Ber.*, 1900, **33**, 1170). Willstätter concluded, therefore, that a *cis-trans*-isomerism, dependent on the relative positions in space of the hydroxyl and methyl groups, existed between tropine and ψ -tropine. Objection to this explanation might be made on the ground that no quite parallel case of isomerism seems to have been observed, and it therefore appeared to the present authors that it should not be accepted unreservedly so long as another explanation is possible.

The tropine molecule contains two similar asymmetric carbon atoms, and the base should therefore be capable of existing in a racemic and an internally compensated form. The possibility of these two optically inactive modifications being represented by tropine and ψ -tropine had been considered by Willstätter, but he rejected this explanation, as both bases, on oxidation, yielded the same ketone. It seemed to the present authors, however, that the possibility of the difference between tropine and ψ -tropine being dependent on the configuration of the two asymmetric carbon atoms was not entirely excluded, for each of these bases might undergo racemisation during the process of oxidation, thus yielding identical ketonic products. Tropinone would then be a mixture of the racemic and meso-ketonic bases, and this would account for its yielding both tropine and ψ -tropine on reduction. On the other

hand, if racemisation does not occur during the oxidation of tropine or ψ -tropine, it was thought possible that two compounds so nearly related as racemic and meso-tropinones might be so similar in properties that their individuality had been overlooked.

In view of the above considerations, therefore, it would appear that the formation of ψ -tropine by the action of sodium amyloxyde on tropine might be a process of racemisation, and this seemed to be in harmony with the experimental facts, since the change in question is never complete. Thus, in our experiments on the preparation of ψ -tropine, about 35 per cent. of the basic product resulting from the treatment with sodium amyloxyde was found to consist of an uncrystallisable mixture of tropine and ψ -tropine, and Willstätter mentions that the yield of pure ψ -base obtained by him did not exceed 50 to 55 per cent. of that theoretically possible. It appeared, therefore, that the action of sodium amyloxyde on tropine resulted in the formation of an equilibrium mixture of this base and ψ -tropine, just as the action of alkali on pilocarpine or isopilocarpine results in the production of an equilibrium mixture of these two stereoisomeric bases (Jowett, *Trans.*, 1905, **87**, 794). This, however, is not the case, since the change is irreversible, no tropine being formed by the action of sodium amyloxyde on ψ -tropine.

Apart from the question of the relation of tropine to ψ -tropine, the individual configuration of each of these bases requires to be established. This point was considered by Gadamer (*Arch. Pharm.*, 1901, **239**, 294), who drew the conclusion that tropine was internally compensated, since hyoscyamine yielded inactive tropine, even when hydrolysed only with water, and he did not consider it likely that a naturally occurring compound would be partially racemic. Much value should not, however, be attached to the grounds on which Gadamer based his conclusions, for partially racemic compounds do occur in nature, as an example of which prulaurasin may be quoted (Hérissey, *Compt. rend.*, 1905, **141**, 959). Moreover, as proved in the present investigation, hyoscyamine always suffers some racemisation when liberated from its salts, and this change might occur in the tropine part of the molecule. That is to say, that if free hyoscyamine were partially racemic, the base, when in the form of its naturally occurring salts, might, nevertheless, be a derivative of optically active tropine.

With the object, therefore, of definitely establishing the configuration of tropine and of ψ -tropine, we have conducted experiments on the resolution of these bases, and some of their derivatives, by fractionally crystallising their salts with certain optically active acids. It may at once be stated that the results of these experi-

ments point to the conclusion that both the bases in question are internally compensated compounds. The relation between them must, therefore, be of the nature of a *cis-trans*-isomerism, as concluded by Willstätter (*loc. cit.*). Attempts were made to racemise tropine by heating the latter at high temperatures with hydrochloric acid, but these were unsuccessful.

ψ -Tropine *d*-camphorsulphonate (m. p. 224—226°) and *d*-bromocamphorsulphonate (m. p. 180°) were prepared and fractionally crystallised, but no evidence of resolution could be obtained. The *normal* and *hydrogen d-tartrates* were also prepared, but these salts could not be crystallised. The *d*-camphorsulphonate (m. p. 176—177°) and *d*-bromocamphorsulphonate (m. p. 190°) of benzoyl- ψ -tropine were then prepared; these salts crystallised well, and were submitted to a prolonged fractionation, but no separation could be effected in either case.

Tropine *d*-camphorsulphonate (m. p. 236°) and benzoyltropine *d*-camphorsulphonate (m. p. 240°) were next investigated, and were found, like the preceding salts, to be incapable of resolution. Finally, tropinone was prepared, both from tropine and from ψ -tropine, and the base obtained from each source was converted into its *d*-camphorsulphonate. The two preparations of tropinone *d*-camphorsulphonate (m. p. 216°) thus obtained were found to be incapable of resolution, and were in all respects identical.

Further and conclusive proof that tropine is an internally compensated compound was obtained by a study of the resolution of atropine. This base is, of course, the tropine ester of *dl*-tropic acid, the latter containing one asymmetric carbon atom. Now, if atropine is a derivative of internally compensated tropine, it would, on resolution, yield only two bases, but if it is derived from racemic tropine, it should be capable of resolution into four stereoisomeric bases, or, at all events, in the latter case, it would be possible to obtain proof of the existence of more than two isomerides. Atropine *d*-camphorsulphonate was therefore prepared, and submitted to fractional crystallisation. It was then found that resolution was readily effected, but the operation yielded only two salts, namely, *d*- and *l*-hyoscyamine *d*-camphorsulphonates. Atropine must therefore contain only one racemic asymmetric carbon atom, namely, that contained in the tropic acid molecule.

l-Hyoscyamine *d*-camphorsulphonate melts at 159°, and the specific rotation of the base contained in it, calculated from that of the salt, is $[\alpha]_D - 32.1^\circ$. This figure is considerably higher than any value previously obtained for the rotation of hyoscyamine, the pure base being usually stated to have about $[\alpha]_D - 21.0^\circ$. It was, however, found impossible directly to obtain from the camphor-

sulphonate a base of higher rotatory power than about $[\alpha]_D - 20.0^\circ$. That this decrease in optical activity was due to the fact that racemisation had occurred was proved by reconvertng the base into the camphorsulphonate, when a rather impure product was obtained, from which, by fractional crystallisation, it was possible to separate the salt of a dextrorotatory base. A preparation of *l*-hyoscyamine having $[\alpha]_D - 25.8^\circ$ was, however, obtained by fractionally crystallising, from an anhydrous solvent, a quantity of the base having $[\alpha]_D - 20.0^\circ$. The ease with which hyoscyamine undergoes racemisation in presence of water is shown by the fact that the rotation diminishes on allowing the base to remain dissolved in moist chloroform. These observations render it evident that no optically pure hyoscyamine has yet been obtained, and that, in all probability, the only salts of this base which have been prepared in a state of purity are those described in the present communication.

d-Hyoscyamine *d*-camphorsulphonate was obtained pure only with considerable difficulty. It melts at 135° , and yields a base possessing properties similar to those of its optical antipode. *d*-Hyoscyamine has not been observed to occur in nature, but it has been obtained synthetically, although only in an impure state. Ladenburg and Hundt (*Ber.*, 1889, **22**, 2590) prepared a base by combining *d*-tropic acid with tropine. This product they called "*d*-atropine," but more recent work has rendered it evident that, in reality, it was impure *d*-hyoscyamine. Amenomiya (*Arch. Pharm.*, 1902, **240**, 498), employing a method similar to that used by Ladenburg and Hundt, prepared a *d*-hyoscyamine of greater purity. This preparation had $[\alpha]_D + 23.0^\circ$ when in the form of its hydrochloride, the latter having been obtained from the aurichloride without liberation of the base. Amenomiya, however, did not determine the rotation of the free base obtained from the salt which he had thus prepared.

Particular interest is attached to the resolution of atropine, inasmuch as it is known that the two stereoisomeric hyoscyamines differ greatly in their respective physiological activities. Thus, Cushny (*J. Physiol.*, 1904, **30**, 176) has shown that *l*-hyoscyamine ($[\alpha]_D - 21.0^\circ$) has about fourteen times the activity of the *d*-hyoscyamine prepared by Amenomiya. The material employed by Cushny was, however, not only partially racemised, but was also, in the case of the *d*-base, extremely limited in amount. A more complete comparison of the physiological actions of the two isomerides has therefore been made by Dr. P. P. Laidlaw, at the Wellcome Physiological Research Laboratories, with the employment of the optically pure *d*-camphorsulphonates obtained

by the resolution of atropine. It has thus been rendered evident that the two optical antipodes have, qualitatively, essentially the same physiological action, and differ only in the intensity of their effects. The ratio of activity of the *l*- to the *d*-isomeride has been found, however, when employing the pure salts, to be much greater than was indicated by Cushny. Thus, the mydriatic action of the former base was found to be about one hundred times that of the latter, whilst the paralysis of the vagus induced by them was in the ratio of 25 : 1, or possibly rather greater.

EXPERIMENTAL.

Tropine.

Tropine d-camphorsulphonate.—This salt is very readily soluble in water or alcohol. It crystallises well, however, from a mixture of alcohol and ethyl acetate, or from chloroform, giving large, tabular crystals, melting at 236°:

0.1138 gave 0.2408 CO₂ and 0.0871 H₂O. C=57.7; H=8.5.

C₈H₁₅ON, C₁₀H₁₆O₄S requires C=57.9; H=8.3 per cent.

The salt was fractionally crystallised under various conditions, but no appreciable difference could be detected between any of the resulting fractions:

0.3761, made up to 25 c.c. with chloroform, gave $\alpha_D + 0^\circ 58'$ in a 2-dcm. tube, whence $[\alpha]_D + 32.1^\circ$.

0.4123, made up to 25 c.c. with water, gave $\alpha_D + 0^\circ 27'$ in a 2-dcm. tube, whence $[\alpha]_D + 13.6^\circ$ and $M_D + 50.6^\circ$.

Benzoyltropine d-camphorsulphonate.—Benzoyltropine was prepared by Ladenburg (*Annalen*, 1883, **217**, 82) by the interaction of tropine and benzoic acid. An improved method of preparation has recently been described by Jowett and Pyman (this vol., p. 1028), who heated tropine hydrochloride with benzoyl chloride, thereby obtaining 77 per cent. of the theoretical yield of benzoyltropine hydrochloride. The present authors, however, found that a practically theoretical yield of the latter salt could be obtained in a few minutes by employing free tropine instead of its hydrochloride. The base was added to an excess of benzoyl chloride, and the mixture heated to the boiling point of the latter. An additive compound of the base and the acid chloride, analogous to the corresponding compound obtained from pyridine, appeared first to be formed, but, when the temperature was raised, this soon re-dissolved, whereupon the hydrochloride of the benzoylated base rapidly separated. The cooled mixture was then diluted with ether, and the hydrochloride collected. After being once crystallised from alcohol, it melted and decomposed at 267° (uncorr.).

Benzoyltropeine d-camphorsulphonate crystallises readily from a mixture of ethyl acetate and alcohol, forming small, flattened needles, which melt at 240° :

0.1131 gave 0.2600 CO_2 and 0.0773 H_2O . $\text{C}=62.7$; $\text{H}=7.6$.

$\text{C}_{15}\text{H}_{19}\text{O}_2\text{N}, \text{C}_{10}\text{H}_{16}\text{O}_4\text{S}$ requires $\text{C}=62.9$; $\text{H}=7.3$ per cent.

0.4012, made up to 20 c.c. with water, gave $\alpha_{\text{D}}+0^{\circ} 26'$ in a 2-dcm. tube, whence $[\alpha]_{\text{D}}+10.8^{\circ}$ and $\text{M}_{\text{D}}+51.5^{\circ}$.

The salt was submitted to a very thorough fractionation, but no resolution could be effected.

ψ -Tropine.

ψ -Tropine was prepared according to the method described by Willstätter (*Ber.*, 1896, **29**, 936). The base was purified by distillation, followed by crystallisation from a mixture of benzene and light petroleum. The mother liquors from the first crystallisation contained a quantity of oily material, amounting to about 35 per cent. of the total product. As this could not be crystallised, it was benzoylated by heating with benzoyl chloride, and the resulting hydrochloride of the benzoylated product crystallised from alcohol. The material thus obtained formed colourless needles, melting at 241° , and appeared to be quite homogeneous; it yielded a picrate melting at 216 — 217° . The product, however, was found to be a mixture of the hydrochlorides of benzoyltropeine and benzoyl- ψ -tropeine, apparently in equal proportions, since, by the addition of successive portions of picric acid solution, it first yielded benzoyltropeine picrate (m. p. 249 — 250°), and finally benzoyl- ψ -tropeine picrate (m. p. 238 — 239°).

ψ -Tropine d-camphorsulphonate.—This salt crystallised readily from a mixture of alcohol and ethyl acetate, forming flat prisms, which were anhydrous, and melted at 224 — 226° :

0.1101 gave 0.2337 CO_2 and 0.0842 H_2O . $\text{C}=57.8$; $\text{H}=8.5$.

$\text{C}_8\text{H}_{15}\text{ON}, \text{C}_{10}\text{H}_{16}\text{O}_4\text{S}$ requires $\text{C}=75.9$; $\text{H}=8.3$ per cent.

ψ -Tropine *d-camphorsulphonate* is very readily soluble in water, ethyl, methyl, and amyl alcohols, and in chloroform, but only very sparingly soluble in ethyl acetate, acetone, benzene, or toluene. It was fractionally crystallised from both cold and boiling solvents, but no evidence of resolution could be obtained:

0.4682, made up to 25 c.c. with alcohol (98 per cent.), gave $\alpha_{\text{D}}+0^{\circ} 59'$ in a 2-dcm. tube, whence $[\alpha]_{\text{D}}+26.3^{\circ}$.

0.4119, made up to 25 c.c. with water, gave $\alpha_{\text{D}}+0^{\circ} 27'$ in a 2-dcm. tube, whence $[\alpha]_{\text{D}}+13.7^{\circ}$ and $\text{M}_{\text{D}}+51.2^{\circ}$.

ψ -Tropine d-bromocamphorsulphonate.—The solubilities of this salt are similar to those of the corresponding *d-camphorsulphonate*.

It is deposited from cool, saturated solutions in large prisms, but separates from a boiling mixture of ethyl acetate and alcohol in fine needles. When anhydrous it melts at 180° , but it separates from moist solvents in needles, which contain one molecule of water of crystallisation, and melt at 112° :

0.9388 of hydrated salt, on heating at 100° , lost $0.0344 \text{ H}_2\text{O}$.
 $\text{H}_2\text{O} = 3.7$.

0.1269 of anhydrous salt gave 0.2229 CO_2 and $0.0788 \text{ H}_2\text{O}$.
 $\text{C} = 47.9$; $\text{H} = 6.9$.

$\text{C}_8\text{H}_{15}\text{ON}, \text{C}_{10}\text{H}_{15}\text{O}_4\text{BrS}, \text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 3.8$ per cent.

$\text{C}_8\text{H}_{15}\text{ON}, \text{C}_{10}\text{H}_{15}\text{O}_4\text{BrS}$ requires $\text{C} = 47.8$; $\text{H} = 6.6$ per cent.

0.4457 of anhydrous salt, made up to 25 c.c. with chloroform, gave $\alpha_D + 2^{\circ} 28'$ in a 2-dcm. tube, whence $[\alpha]_D + 69.1^{\circ}$.

0.5030 of anhydrous salt, made up to 25 c.c. with water, gave $\alpha_D + 2^{\circ} 26'$ in a 2-dcm. tube, whence $[\alpha]_D + 60.5^{\circ}$ and $M_D + 273.3^{\circ}$.

Prolonged fractional crystallisation of this salt gave no evidence of resolution.

Benzoyl- ψ -tropine d-camphorsulphonate. — Benzoyl- ψ -tropine (tropacocaine) was prepared in a manner similar to that employed for the preparation of benzoyltropine; the yield was practically quantitative. The hydrochloride of the base was found to melt at 283° (uncorr.), a temperature 12° higher than that recorded by Liebermann (*loc. cit.*) and by Willstätter (*loc. cit.*) for the melting point of benzoyl- ψ -tropine (tropacocaine) hydrochloride. The aurichloride melted at 208° , and was analysed:

0.1391 gave 0.0468 Au . $\text{Au} = 33.6$.

$\text{C}_{15}\text{H}_{19}\text{O}_2\text{N}, \text{HAuCl}_4$ requires $\text{Au} = 33.7$ per cent.

Benzoyl- ψ -tropine d-camphorsulphonate crystallises very readily from a mixture of ethyl acetate and alcohol, forming large prisms, melting at 176 — 177° :

0.1236 gave 0.2846 CO_2 and $0.0823 \text{ H}_2\text{O}$. $\text{C} = 62.8$; $\text{H} = 7.4$.

$\text{C}_{15}\text{H}_{19}\text{O}_2\text{N}, \text{C}_{10}\text{H}_{16}\text{O}_4\text{S}$ requires $\text{C} = 62.9$; $\text{H} = 7.3$ per cent.

0.5412, made up to 20 c.c. with water, gave $\alpha_D + 0^{\circ} 36'$ in a 2-dcm. tube, whence $[\alpha]_D + 11.1^{\circ}$ and $M_D + 51.8^{\circ}$.

The salt was separated into a large number of fractions, but no evidence of resolution could be obtained.

Benzoyl- ψ -tropine d-bromocamphorsulphonate.—This salt differs from the sulphonates above described, inasmuch as it forms a hydrate which is only sparingly soluble in cold water. This compound forms slender needles, which melt at 73° :

0.5420, on drying at 123° , lost $0.0464 \text{ H}_2\text{O}$. $\text{H}_2\text{O} = 8.6$.

$\text{C}_{17}\text{H}_{19}\text{O}_2\text{N}, \text{C}_{10}\text{H}_{15}\text{O}_4\text{BrS}, 3\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 8.8$ per cent.

The anhydrous salt crystallises readily from a mixture of ethyl acetate and alcohol, and forms thin prisms, which melt at 190° :

0.1401 gave 0.2779 CO_2 and 0.0794 H_2O . C = 54.1; H = 6.3.

$\text{C}_{15}\text{H}_{19}\text{O}_2\text{N}, \text{C}_{10}\text{H}_{15}\text{O}_4\text{BrS}$ requires C = 54.0; H = 6.1 per cent.

0.4827, made up to 20 c.c. with water, gave $\alpha_D + 2^{\circ} 17'$ in a 2-dm. tube, whence $[\alpha]_D + 47.3^{\circ}$ and $M_D + 262.9^{\circ}$.

This result for the molecular rotatory power is rather lower than would have been expected for the bromocamphorsulphonate of an inactive base. Nevertheless, the base was devoid of optical activity, and the discrepancy can only be ascribed to the fact that the solutions examined were highly supersaturated. The salt was separated by crystallisation into a number of fractions, but all of these had the same rotatory power and melting point.

Tropinone.

Tropine and ψ -tropine were each separately oxidised to tropinone, according to the method described by Willstätter (*Ber.*, 1896, **29**, 393), and the resulting base purified by means of the picrate. Willstätter states that this salt melts at 220° , but the present authors find that the temperature of fusion is dependent on the rate of heating, and may lie at any point from 210 — 250° . Each preparation of the base was converted into the *d*-camphorsulphonate, when the resulting salts were found to be in all respects identical.

Tropinone *d*-camphorsulphonate is fairly readily soluble in dry ethyl acetate, from which it crystallises in moss-like growths, apparently composed of needles; it melts and decomposes at 216° :

0.1130 gave 0.2421 CO_2 and 0.0830 H_2O . C = 58.4; H = 8.1.

$\text{C}_8\text{H}_{13}\text{ON}, \text{C}_{10}\text{H}_{16}\text{O}_4\text{S}$ requires C = 58.2; H = 7.9 per cent.

The salt is much less soluble in ethyl acetate which has not been specially dried, and crystallises from this solvent in tufts of leaflets, which, when rapidly heated, suddenly lose water of crystallisation at 140° , but without completely melting:

2.0429, on heating at 123° , lost 0.0939 H_2O . $\text{H}_2\text{O} = 4.6$.

$\text{C}_8\text{H}_{13}\text{ON}, \text{C}_{10}\text{H}_{16}\text{O}_4\text{S}, \text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 4.6$ per cent.

The hydrated salt appears to be dimorphous, since, at low temperatures, it crystallises from a mixture of ethyl acetate and dilute alcohol in long, slender prisms.

No resolution of tropinone *d*-camphorsulphonate could be effected by fractional crystallisation.

The Resolution of Atropine.

Forty grams of atropine were neutralised with *d*-camphorsulphonic acid, and the resulting salt was fractionally crystallised from ethyl acetate containing some alcohol. The first crop of crystals consisted of prismatic needles, and melted at 136—140°. This was recrystallised several times until no further change occurred; it then melted at 159°.

0.5072, made up to 25 c.c. with water, gave $\alpha_D - 0^\circ 19.5'$ in a 2-dcm. tube, whence $[\alpha]_D - 8.0^\circ$ and $M_D - 41.7^\circ$.

Since the molecular rotation of *d*-camphorsulphonic acid is $+51^\circ$, it is evident that the basic ion of the above salt has $M_D - 92.7^\circ$, which corresponds with a specific rotatory power of -32.1° . It is seen, therefore, that resolution had been effected, and that the salt melting at 159° was *l*-hyoscyamine *d*-camphorsulphonate:

0.1302 gave 0.2974 CO₂ and 0.0902 H₂O. C = 62.3; H = 7.7.

C₁₇H₂₃O₃N, C₁₀H₁₆O₄S requires C = 62.4; H = 7.5 per cent.

For the purpose of comparison a quantity of natural *l*-hyoscyamine was converted into the *d*-camphorsulphonate. The salt so obtained melted at 149—150°, and was somewhat impure; after recrystallisation, however, it melted at 159°, and was identical with the salt obtained from atropine. *l*-Hyoscyamine *d*-camphorsulphonate is extremely readily soluble in water, alcohol, or chloroform, and very sparingly soluble in ethyl acetate, benzene, or xylene. The material contained in the mother liquors obtained during the separation of the *l*-hyoscyamine *d*-camphorsulphonate from the original atropine salt, which would contain the salt of *d*-hyoscyamine, was submitted to a very elaborate process of fractional crystallisation, whereby it was shown conclusively that the salts of only two bases were present. The product did not crystallise readily, and exhibited a considerable tendency to separate as an oil. After a large number of crystallisations, however, the salt of the *d*-base was obtained in a state of purity.

d-Hyoscyamine *d*-camphorsulphonate forms small needles, which melt at 135°. Its solubilities are similar to, but rather greater than, those of the corresponding lævo-salt:

0.1212 gave 0.2793 CO₂ and 0.0840 H₂O. C = 62.1; H = 7.7.

C₁₇H₂₃O₃N, C₁₀H₁₆O₄S requires C = 62.4; H = 7.5 per cent.

0.5229, made up to 20 c.c. with water, gave $\alpha_D + 1^\circ 25.5'$ in a 2-dcm. tube, whence $[\alpha]_D + 27.25^\circ$ and $M_D + 143.7^\circ$.

From this result it is calculated that the basic ion has $M_D + 92.7^\circ$ and $[\alpha]_D + 32.1^\circ$, figures which are in exact agreement with the corresponding values obtained for the *l*-base.

It would appear, therefore, that the respective bases contained in the above-described pure *d*-camphorsulphonates have a specific rotation of $[\alpha]_D \pm 32.1^\circ$, a value considerably higher than that usually given for hyoscyamine (about -21.0°). It was, however, found impossible to obtain directly from either of the camphorsulphonates in question a base of higher specific rotatory power than about $[\alpha]_D \pm 20.0^\circ$, even when the greatest care was taken to avoid racemisation. That this change, nevertheless, had occurred to some extent was shown by reconverting a quantity of the base having $[\alpha]_D - 20.0^\circ$ into the *d*-camphorsulphonate, when a somewhat impure salt was obtained, from which the derivative of a dextro-base was separated. A considerable quantity of the lævo-base, having $[\alpha]_D - 20.2^\circ$, was fractionally crystallised from petroleum (b. p. $90-120^\circ$), when a fraction was eventually obtained which melted at $107-108^\circ$, and had the following rotatory power:

0.4331, made up to 20 c.c. with 50 per cent. alcohol, gave $\alpha_D - 1^\circ 7'$ in a 2-dcm. tube, whence $[\alpha]_D - 25.8^\circ$.

This is a higher value than has heretofore been observed for the rotation of hyoscyamine.

d-Hyoscyamine, obtained from its *d*-camphorsulphonate, was in all respects analogous to its optical antipode.

As it appears probable from the above results that optically pure hyoscyamines have never been obtained in a free state, several salts of these bases were prepared by double decomposition from the pure *d*-camphorsulphonates. Corresponding salts of atropine have also been made for the purpose of comparison.

The Aurichlorides.—*l*-Hyoscyamine aurichloride has previously been described as forming leaflets, melting at 162° (Will, *Ber.*, 1888, **21**, 1717). The pure salt forms golden-yellow, hexagonal plates, which melt at 165° , and are anhydrous:

0.1244 gave 0.0391 Au. Au = 31.35.

$C_{17}H_{23}O_3N.HAuCl_4$ requires Au = 31.35 per cent.

l-Hyoscyamine aurichloride is much more soluble in alcohol than in water, but can readily be crystallised from the former solvent.

Somewhat impure *d*-hyoscyamine aurichloride was prepared by Amenomiya (*loc. cit.*). The pure salt crystallises similarly to its optical antipode, melts at 165° , and is anhydrous:

0.1198 gave 0.0374 Au. Au = 31.22.

$C_{17}H_{23}O_3N.HAuCl_4$ requires Au = 31.35 per cent.

Atropine aurichloride showed some tendency to separate as an oil, but crystallised fairly readily. It formed tufts of very small, anhydrous leaflets, which melted at $134-139^\circ$:

0.0926 gave 0.0292 Au. Au = 31.5.

$C_{17}H_{23}O_3N.HAuCl_4$ requires Au = 31.35 per cent.

The Auribromides.—*l*-Hyoscyamine auribromide was first prepared by Jowett (Trans., 1897, 71, 679), who stated that it melts at 115—120°, and regarded it as being anhydrous. The present authors find that the pure salt separates from water with one molecule of water of crystallisation, and, when dried in the air, melts at about 123—130°. The anhydrous salt, on heating, sinters slightly at 155°, after which it fuses sharply at 160°, without decomposition. The salt is even more sparingly soluble in water than the corresponding aurichloride, and crystallises in very long, highly lustrous, flattened needles, possessing a deep red colour. It dissolves much more readily in absolute alcohol than in water, and crystallises from the former solvent with one molecule of alcohol:

2·0350, crystallised from water, on heating at 110°, lost 0·0418 H₂O. H₂O=2·1.

0·3029, crystallised from alcohol, on heating at 110°, lost 0·0158 EtOH. EtOH=5·2.

0·1210 of anhydrous salt gave 0·0294 Au. Au=24·3.

C₁₇H₂₃O₃N,HAuBr₄,H₂O requires H₂O=2·2 per cent.

C₁₇H₂₃O₃N,HAuBr₄,EtOH „ EtOH=5·4 „

C₁₇H₂₃O₃N,HAuBr₄ „ Au=24·3 „

d-Hyoscyamine auribromide has not previously been obtained. It agrees in all respects with the description of the corresponding lævo-salt given above:

0·2197 of hydrated salt, on heating at 110°, lost 0·0044 H₂O. H₂O=2·0.

0·0966 of anhydrous salt gave 0·0235 Au. Au=24·3.

C₁₇H₂₃O₃N,HAuBr₄,H₂O requires H₂O=2·2 per cent.

C₁₇H₂₃O₃N,HAuBr₄ „ Au=24·3 „

Atropine auribromide was described by Jowett (*loc. cit.*), who considered it to be anhydrous, and stated that it crystallised in chocolate-coloured prisms melting at 120°. The salt, as prepared by the present authors, does not crystallise nearly so readily as the corresponding derivatives of the hyoscyamines. It forms very small tufts of dark red needles, which contain one molecule of water of crystallisation, and, when air dried, forms a crystalline powder, melting at 110°. The anhydrous salt fuses at 120°:

0·1225, on heating at 100°, lost 0·0027 H₂O. H₂O=2·2.

0·1082 of anhydrous salt gave 0·0263 Au. Au=24·3.

C₁₇H₂₃O₃N,HAuBr₄,H₂O requires H₂O=2·2 per cent.

C₁₇H₂₃O₃N,HAuBr₄ „ Au=24·3 „

The Picrates.—The picrates of *l*-hyoscyamine and atropine are mentioned in the literature, but their melting points have not been recorded. *d*-Hyoscyamine picrate has not previously been prepared.

Both *d*- and *l*-hyoscyamine picrates crystallise fairly readily, forming needles, which melt at 163°, without decomposition. Atropine picrate crystallises much more readily than the corresponding salts of either of the active bases, and forms rectangular plates, which melt at 173—174°.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C.

CCXVII.—*Synthesis of Cotarnic Acid.*

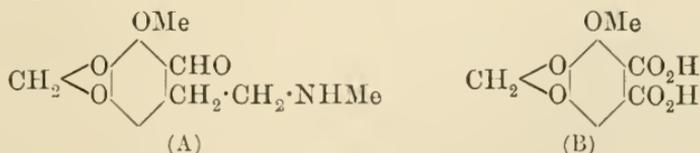
By WILLIAM HENRY PERKIN, jun., ROBERT ROBINSON, and FREDERICK THOMAS.

DURING the course of an investigation on narcotin and its degradation products, on which we have been engaged for a considerable time, we have carried out a series of experiments which have resulted in a synthesis of cotarnic acid, and have thus definitely established the constitution of this important acid.

Wöhler (*Annalen*, 1844, 50, 19) first obtained cotarnine, $C_{12}H_{15}O_4N$, from narcotin, $C_{22}H_{23}O_7N$, by oxidation with manganese dioxide and dilute sulphuric acid, and the careful investigation of this important substance has shown that it is probably an aldehyde of the constitution :



Furthermore, the experiments of Freund and Becker (*Ber.*, 1903, 36, 1521) have made it probable that the methoxy-group in cotarnine is adjacent to the aldehyde group, and the above formula may therefore be expanded to (A) :



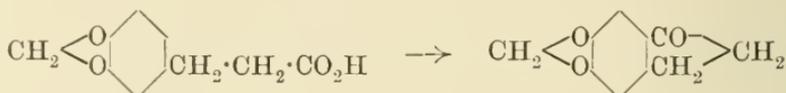
When cotarnine is oxidised with permanganate, it yields cotarnic acid, $C_{10}H_8O_7$, and if the constitution for cotarnine just given is accepted as correct, the constitution of cotarnic acid will be represented by the formula (B), and this acid is therefore methoxy-hydrastic acid.

The highly ingenious method which Freund and Becker have employed to show that cotarnine is a derivative both of piperonal and

of salicylaldehyde methyl ether, as indicated in the formula just mentioned, does not appear to us to be quite conclusive, and we have therefore confirmed this formula by synthesising cotarnic acid by a method which leaves no room for doubt as to its constitution.

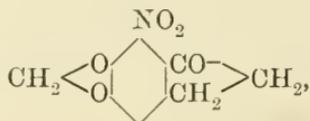
The synthesis proved to be a difficult one, but after many unsuccessful attempts in other directions, we ultimately succeeded in solving the problem by a process which is briefly as follows :

The starting point was 5 : 6-methylenedioxy-1-hydrindone, which we prepared in quantity from 3 : 4-methylenedioxyphenylpropionic acid by the action of phosphoric oxide :



(compare Perkin and Robinson, *Trans.*, 1907, **91**, 1084).

When this substance is treated with concentrated nitric acid, it is readily converted into 7-nitro-5 : 6-methylenedioxy-1-hydrindone (m. p. 164—165°),



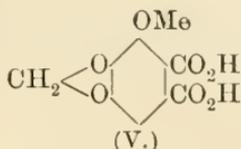
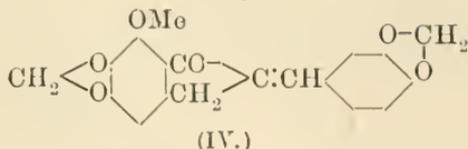
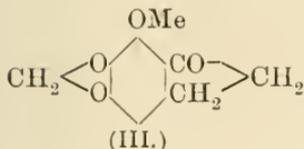
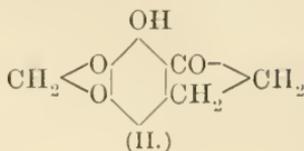
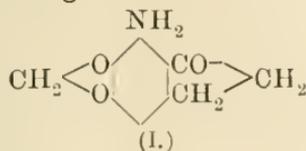
and this is reduced by tin and hydrochloric acid with formation of the corresponding amino-derivative, m. p. 175° (I). The next step was to convert the amino-derivative into 7-hydroxy-5 : 6-methylenedioxy-1-hydrindone (II) by diazotisation, and although, owing to the formation of brown by-products, the yield of the hydroxy-derivative was very small, we succeeded in obtaining sufficient for our purpose.

This hydroxy-derivative yields an intense violet coloration on the addition of ferric chloride to the alcoholic solution, and the hydroxy-group is therefore most probably adjacent to the carbonyl group. It was for this reason that we assign the position 7 to the nitro-group in 7-nitro-5 : 6-methylenedioxy-1-hydrindone.

By treatment in alkaline solution with methyl sulphate, the hydroxy-derivative was next converted into the corresponding methoxy-derivative (III), and this, when condensed with piperonal and dilute aqueous potassium hydroxide, yielded 7-methoxy-5 : 6-methylenedioxy-2-piperonylidene-1-hydrindone (m. p. 225—230°, IV).

This piperonylidene derivative was oxidised by permanganate, and the acid produced was recognised as cotarnic acid (V) by conversion into the characteristic methylimide, which melted at 205°, and had the same properties as a specimen of the methylimide of cotarnic acid which we prepared from cotarnic acid obtained by the oxidation of

cotarnine. The steps in this synthesis of cotarnic acid are therefore the following :



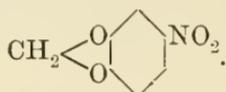
The yield of cotarnic acid obtained in this way is, unfortunately, very small, and we are engaged in an attempt to discover a more satisfactory method of synthesis.

Nitration of the Methylene Ether of Catechol.

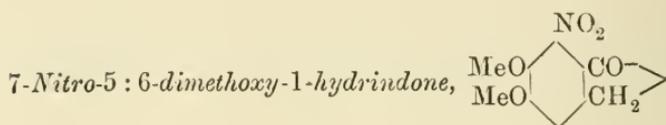
The methylene ether of catechol has been prepared by Moureu (*Bull. Soc. chim.*, 1896, [iii], 15, 654) by the action of methylene iodide on the sodium derivative of catechol. Since we wished to investigate the constitution of its mononitro-derivative, we have endeavoured to use the cheaper methylene chloride in its preparation, and we find that the methylene ether can be so produced, but the yield is very unsatisfactory. Catechol (66 grams) was dissolved in absolute alcohol and mixed with a solution of sodium (27.6 grams) in alcohol and methylene chloride (50 grams). After boiling for sixteen hours in a reflux apparatus, the bulk of the alcohol was distilled off, water was then added, the oil extracted with ether, and the ethereal solution dried and evaporated. The residue consisted almost entirely of an oil which distilled at 170—175° under the ordinary pressure, whereas the boiling point of the methylene ether of catechol is stated by Moureu (*loc. cit.*) to be 172—173°. A small quantity of this substance was dissolved in glacial acetic acid and treated with a little nitric acid, when the nitro-derivative separated and, after crystallisation from alcohol, had the correct melting point, 147°. Its constitution was proved as follows: The nitro-compound was readily reduced by tin and hydrochloric acid, and the resulting base was obtained by rendering the solution alkaline with potassium hydroxide and extracting with ether. The base was converted, by warming with acetic anhydride,

into the acetylamino-compound, which crystallised from water in colourless needles and melted at 135° .

Since the melting point was unaltered by admixture with the acetylamino-derivative of the methylene ether of catechol, which is obtained by the successive action of potassium hypobromite and acetic anhydride on the amide of piperonylic acid, it is clear that the nitro-compound produced by the nitration of the methylene ether of catechol is *4-nitro-1:2-methylenedioxybenzene*,



Salway (this vol., 1155) has already shown that one of the products of the nitration of piperonal has the same constitution.



In order to prepare this substance, 5:6-dimethoxyhydrindone (Perkin and Robinson, *Trans.*, 1907, **92**, 1092, 2 grams) was stirred vigorously with nitric acid (D 1.42, 10 c.c.), when the whole dissolved, and, if the hydrindone was quite pure, no oxidation occurred.

After adding water, the sticky mass which separated gradually became hard, and was collected and washed with water.

This nitro-compound crystallises from a mixture of ethyl acetate and light petroleum in pale yellow prisms, or from methyl alcohol, in which it is very sparingly soluble in the cold, in almost colourless, prismatic needles. If the hot saturated solution in methyl alcohol is rapidly cooled, needles separate, and after some time these change into prisms :

0.1681 gave 8.4 c.c. N_2 at 15° and 771 mm. $N = 6.0$.

$C_{11}H_{11}O_5N$ requires $N = 5.9$ per cent.

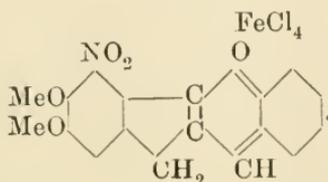
7-Nitro-5:6-dimethoxy-1-hydrindone melts at $149-150^{\circ}$, and, as the following experiments show, exhibits the characteristic properties of a derivative of hydrindone. (I) The solution in hot methyl alcohol was treated with piperonal and a little potassium hydroxide, when a yellow colour was immediately produced and a canary-yellow, crystalline precipitate of the piperonylidene derivative quickly separated. This substance may be recrystallised by adding methyl alcohol to its solution in hot pyridine, and the pale yellow prisms thus obtained melt at 260° with slight previous darkening. The colour of its solution in concentrated sulphuric acid is intense reddish-purple, and becomes yellow on dilution with water:

(II) Approximately equal weights of the nitro-hydrindone and of salicylaldehyde were dissolved in methyl alcohol, and a rapid stream of hydrogen chloride passed through the solution for a minute.

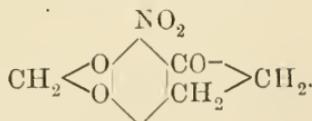
On cooling, brick-red crystals of the oxonium anhydro-hydrochloride separated from the solution. This salt dissolves in water or concentrated sulphuric acid to yellow solutions which do not fluoresce.

The double salt with platinic chloride crystallises in orange, microscopic needles. The anhydro-ferrichloride melts at 188°, and is a brick-red precipitate, which crystallises from glacial acetic acid in orange-brown needles with characteristic prismatic edges.

This ferrichloride has analogous properties to the similarly constituted substances already described by Perkin, Robinson and Turner (Trans., 1908, 93, 1085), and there can be little doubt that it has the constitution



7-Nitro-5:6-methylenedioxy-1-hydrindone,



This substance may be prepared by adding nitric acid (D 1.42, 15 c.c.), previously boiled to remove nitrous acid, to 5:6-methylenedioxy-1-hydrindone (Trans., 1907, 91, 1084). The hydrindone dissolves and, after two minutes, water is added, and the precipitated nitro-compound, which rapidly hardens, is collected, washed, dried, and then purified by repeated extraction with boiling light petroleum (b. p. 60—70°):

0.1507 gave 8.5 c.c. N_2 at 10° and 749 mm. $N = 6.6$.

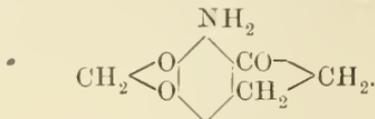
$C_{10}H_7O_5N$ requires $N = 6.3$ per cent.

7-Nitro-5:6-methylenedioxy-1-hydrindone melts at 164—165°, and, if pure hydrindone was employed in its preparation, it may be readily crystallised from methyl alcohol, from which it separates in very pale elongated prisms. The colour of the solution in sulphuric acid is only pale yellow, which is rather remarkable in view of the fact that 5:6-methylenedioxyhydrindone itself dissolves in sulphuric acid with an intense red coloration.

The piperonylidene derivative, prepared in the usual way, separates in lemon-yellow, microscopic needles, which are very sparingly soluble in alcohol and melt at 290° with decomposition. It is soluble in boil-

ing glacial acetic acid, and, on the addition of hydrochloric acid, a red colour is produced, which disappears as the substance crystallises from the solution. The colour of the solution of the piperonylidene derivative in sulphuric acid is purple.

7-Amino-5 : 6-methylenedioxy-1-hydrindone,

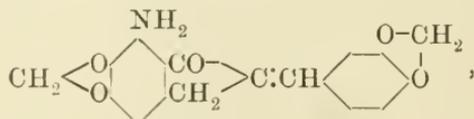


The reduction of 7-nitro-5 : 6-methylenedioxy-1-hydrindone to the corresponding amino-derivative may be carried out by gently boiling its alcoholic solution for two hours with alcohol (200 c.c.) and hydrochloric acid (22.5 c.c.) with excess of tin. The product is then poured into dilute hydrochloric acid, filtered hot from insoluble matter, and the tin eliminated by treatment with hydrogen sulphide. As soon as the liquid smells strongly, it is filtered, and the clear solution rendered alkaline with sodium hydroxide, when a finely divided precipitate separates, which is collected, dried on porous porcelain, and crystallised from methyl alcohol. Owing to the various by-products, the yield was, unfortunately, only about 10 per cent. of that theoretically possible :

0.1612 gave 10.4 c.c. N_2 at 13° and 746 mm. $N = 7.5$.

$C_{10}H_9O_3N$ requires $N = 7.3$ per cent.

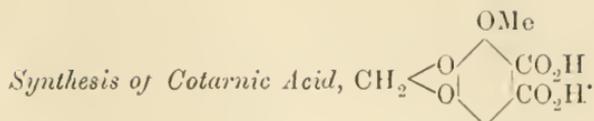
7-Amino-5 : 6-methylenedioxy-1-hydrindone separates from methyl alcohol in colourless needles, and melts at 175° . It yields, with piperonal and alcoholic potassium hydroxide, a bright yellow, crystalline piperonylidene derivative, which doubtless has the constitution



since, on treatment with sodium nitrite and hydrochloric acid in excess of alcohol, a solution is obtained which gives a red coloration with alkaline β -naphthol. Aminomethylenedioxyhydrindone dissolves slowly in dilute hydrochloric acid, and the colourless solution becomes yellow on the addition of sodium nitrite.

On adding this to an alkaline solution of β -naphthol, a crimson solution is obtained, from which a scarlet azo-compound separates.

This azo-compound dissolves in concentrated sulphuric acid with an intense indigo-blue colour.



The conversion of 7-amino-5:6-methylenedioxy-1-hydrindone into cotarnic acid proved to be a much more difficult operation than was expected, owing principally to the formation, even under the best conditions, of large quantities of other substances and consequent small yield of the acid. After several comparative experiments, the synthesis was ultimately accomplished in the following way.

Aminomethylenedioxyhydrindone (10 grams) was dissolved in the least possible quantity of warm dilute hydrochloric acid and cooled with ice, when some of the hydrochloride of the base separated.

Sodium nitrite (3.5 grams), dissolved in a little water, was then added, the solution vigorously boiled for ten minutes, filtered, saturated with ammonium sulphate, and repeatedly extracted with ether.

The solution, mixed with alcohol, gave an intense violet coloration* on the addition of ferric chloride, indicating that the hydroxy-methylenedioxyhydrindone produced probably contains a hydroxy-group in the ortho-position with respect to the carbonyl group (compare p. 1978). Unfortunately, the conversion of the amino- into the hydroxy-group is always accompanied by the formation of an insoluble, brown substance, which could not be crystallised, and greatly affects the yield of the hydroxy-derivative. The ethereal solution of the hydroxy-derivative was extracted with small quantities of dilute potassium hydroxide, and the alkaline solutions agitated in the cold with methyl sulphate in excess. When all the methyl sulphate had been decomposed, the solution was extracted with ether and the ethereal solution evaporated. The residue showed a tendency to crystallise, but, as the whole of the material was required for the synthesis, the product was not directly investigated, but, at once, dissolved in alcohol and treated with piperonal and some dilute potassium hydroxide. The yellow precipitate so obtained undoubtedly consists of *7-methoxy-5:6-methylenedioxy-2-piperonylidene-1-hydrindone* (IV, p. 1979).

It may be crystallised from a mixture of pyridine and alcohol, melts at 225—230°, and dissolves in sulphuric acid, yielding an intense carmine solution. The substance obtained from five of the above operations was oxidised, at as low a temperature as possible, with

* On one occasion, the reaction, for some unknown reason, proceeded in another direction, and the ether extract contained a substance which yielded a green coloration with ferric chloride.

potassium permanganate containing a small quantity of potassium carbonate, but oxidation proceeded, especially at first, with difficulty, owing largely to the insolubility of the substance. After a considerable amount of permanganate had been reduced, the solution was boiled, filtered, the manganese precipitate treated with hot water and sulphur dioxide, and the unchanged piperonylidene derivative collected and again oxidised with permanganate, the operation being repeated until only a negligible amount remained unoxidised.

The alkaline filtrates from the manganese precipitates were combined, evaporated to a small bulk, the solution was then rendered acid to Congo-paper, and the small quantity of piperonylic acid which separated removed by filtration. The filtrate was evaporated to dryness, extracted with pure dry ether in a Soxhlet apparatus, and, after distilling off the ether, a small quantity of a syrupy acid remained, which quickly crystallised, apparently in plates. The quantity was so small that an analysis was not attempted, and as the melting point of cotarnic acid is not sufficiently decisive, the whole was converted into the methylimide which we had previously prepared from a specimen of cotarnic acid from cotarnine and found to be highly characteristic. In this experiment, the crude acid was dissolved in a little hot water, when it was noticed that the solution, on cooling, deposited crystals exactly resembling those of cotarnic acid. Excess of methylamine was now added, the solution evaporated to dryness on the water-bath, and the methylamine salt heated in a test-tube, when a sublimate of needles was obtained and an oil distilled which soon solidified. The distillate and sublimate were dissolved in a little boiling methyl alcohol, when the filtered solution deposited a crop of almost colourless needles, which melted at 205° , and had all the properties of the methylimide of cotarnic acid, the identity with which was further confirmed by the fact that an intimate mixture of the two preparations melted sharply at 205° . There can thus be no doubt that the substance synthesised in the experiments described above was cotarnic acid.

THE UNIVERSITY,
MANCHESTER.

CCXVIII.—*The Constituents of the Fruit of Ecballium Elaterium.*

By FREDERICK BELDING POWER and CHARLES WATSON MOORE.

IN a recent communication by the authors, entitled "Chemical Examination of Elaterium and the Characters of Elaterin" (*Pharm. J.*, 1909, [iv], 29, 501), it was shown that the product known and officially recognised as "elaterin" is not homogeneous, but that it consists, to the extent of 60—80 per cent., of a crystalline substance which is completely devoid of the specific physiological action attributed to elaterin, and may be separated by a process of fractional crystallisation. This crystalline substance, which is much more highly levorotatory and has a higher melting point than the crude elaterin, is accompanied in the latter by a compound of apparently the same percentage composition, but which possesses a very high degree of physiological activity and is dextrorotatory.

In view of the fact that the elaterium from which the above-mentioned "elaterin" is obtained represents only the material which is deposited from the juice of the fruit of *Ecballium Elaterium*, it appeared desirable that the entire fresh fruit should be subjected to a chemical examination in order to ascertain the nature of all its constituents. In conducting this investigation, special consideration has been given to the statement of Berg (*Bull. Soc. chim.*, 1897, [iii], 17, 85) that elaterin does not pre-exist in the fruits of *Ecballium*, but that it is formed, after the expression of the juice, by the action of a ferment on an amorphous glucoside. The results which have now been obtained, with the deductions from them, are summarised at the end of this paper.

EXPERIMENTAL.

The material employed in this investigation consisted of the fresh, nearly ripe fruits of *Ecballium Elaterium*, A. Richard, which were very kindly supplied to us by Messrs. W. Ransom & Son, of Hitchin. They were collected during the latter part of August.

Separation of an Enzyme.

It has been indicated by Berg (*loc. cit.*) that the juice of the fruit of *Ecballium* contains an enzyme, or possibly a mixture of enzymes, which is capable of hydrolysing amygdalin, saccharose, and starch, and was designated by him as elaterase. In order to obtain this substance, the expressed juice from 3 kilograms of the fruit, amount-

ing to about 900 c.c., was filtered, and mixed with 1500 c.c. of strong alcohol. A voluminous, light-coloured, amorphous precipitate was thus produced, which was collected, washed with a little alcohol, and dried, when it amounted to 1.5 grams. The product was readily soluble in cold water, and, although containing a large proportion of inorganic material, rapidly hydrolysed β -glucosides.

Extraction of the Fruit with Alcohol.

For the purpose of a complete examination, 27 kilograms of the fruit were employed.

With consideration of the statement by Berg (*loc. cit.*) that the elaterin contained in the fruit of *Ecballium* exists in the form of a glucoside which is readily hydrolysed by the enzyme present, the material was treated in such a manner as to preclude the possibility of any hydrolysis of its constituents taking place. Each fruit, therefore, was separately cut into several pieces, which were allowed to fall directly into strong alcohol, the total volume of the latter having been about 80 litres. After a short time, the mixture was heated to the boiling point, and kept at this temperature for about fifteen minutes. The whole was subsequently kept overnight, after which the marc was removed by filtration, the liquid thus obtained being then found to contain slightly over 75 per cent. by volume of alcohol.

The marc, separated by filtration as above described, was pressed, and the liquid thus obtained was added to the main portion of alcoholic extract. The seeds were then separated so far as possible from the pressed marc, and the latter completely extracted in a Soxhlet apparatus with hot alcohol, this extract being likewise added to that first obtained. The united liquids were then concentrated by distillation from a water-bath until alcohol ceased to pass over.

During the concentration of the alcoholic extract, as above described, there separated a quantity of green resin (A), which was collected on a filter and repeatedly treated with water until nothing further was removed. The filtrate and washings from this resin were united, and concentrated under diminished pressure to a volume of about 3 litres. During this operation a quantity of light brown, resinous material (B) separated, which was collected and thoroughly washed with cold water the washings being added to the aqueous liquid (C).

Examination of the Green Resin (A).

This product was a dark green, soft mass, and amounted to 45.5 grams. It was dissolved in alcohol, and mixed with purified sawdust, the thoroughly-dried mixture being then successively extracted in a Soxhlet apparatus with light petroleum (b. p. 35—50°), ether, chloroform, and alcohol.

Petroleum Extract of the Green Resin.

This extract was a dark green, viscid liquid, and amounted to 38 grams. It was dissolved in ether, the ethereal liquid being shaken successively with solutions of sodium carbonate and sodium hydroxide, but nothing was thus removed. The ether was then evaporated, and the residue hydrolysed by heating with an alcoholic solution of potassium hydroxide, after which the alcohol was removed, water added, and the alkaline solution of potassium salts extracted with ether. The ethereal liquid was washed, dried, and the solvent removed, when a small quantity of a light brown, crystalline product was obtained. This was dissolved in about 150 c.c. of hot absolute alcohol, and the solution kept for some time, when a nearly colourless substance separated. The latter was collected, washed with cold alcohol, and then distilled under 15 mm. pressure. The distillate, which rapidly solidified, was crystallised from ethyl acetate, when small, colourless, glistening leaflets, melting at 68° , were obtained. This substance was a hydrocarbon, and appeared to be hentriacontane, $C_{31}H_{64}$, but the amount was too small for analysis.

Isolation of a Phytosterol, $C_{27}H_{46}O$.

The alcoholic solution from which the hydrocarbon had been removed by filtration, as above described, was concentrated to a small volume and diluted with water, when a quantity of crystalline substance separated. This was collected on a filter, and washed with a little ethyl acetate, after which it was distilled under diminished pressure. The distillate, which solidified on cooling, was crystallised from a mixture of ethyl acetate and dilute alcohol, when it formed colourless, glistening leaflets melting at 148° . The amount of substance so obtained was 0.7 gram :

0.2806, heated at 115° , lost 0.0134 H_2O . $H_2O = 4.8$.

0.1342 of anhydrous substance gave 0.4125 CO_2 and 0.1430 H_2O .

$C = 83.8$; $H = 11.8$.

$C_{27}H_{46}O, H_2O$ requires $H_2O = 4.5$ per cent.

$C_{27}H_{46}O$ requires $C = 83.9$; $H = 11.9$ per cent.

The substance thus agrees in composition with a phytosterol, and it yielded the colour reactions of this class of compounds. A determination of its specific rotatory power gave the following result :

0.2055, made up to 20 c.c. with chloroform, gave $a_D + 0.4'$ in a 2-dcm. tube, whence $[\alpha]_D + 3.2^{\circ}$.

The acetyl derivative, when crystallised from acetic anhydride, separated in flat, glistening needles, melting at $155-157^{\circ}$.

The above-described phytosterol differs appreciably in some of its characters from the commonly-occurring substances of this class, as indicated, for example, by its higher melting point, its dextrorotation, and the fact that the acetyl derivative melts higher than the substance from which it was prepared.

The aqueous alkaline solution of potassium salts from which the hydrocarbon and phytosterol had been removed by extraction with ether, as above described, was acidified, and again extracted with ether. The ethereal liquid obtained in this way contained a small amount of a nearly colourless, very sparingly soluble substance in suspension. This was collected on a filter, washed with ether, and crystallised from pyridine, when it formed small, glistening plates, melting at 258—260°. It appears to be related to ipuranol, $C_{23}H_{35}O_2(OH)_2$, as it gives the characteristic colour reactions of this substance, but the amount obtained was insufficient for analysis (compare *Amer. J. Pharm.*, 1908, 80, 264, 576; *Trans.*, 1908, 93, 907; this vol., p. 249).

Examination of the Fatty Acids.

The ethereal liquid, from which the above-described substance had been separated, was washed, dried, and the solvent removed. A quantity (12 grams) of fatty acids was thus obtained, which, when distilled under diminished pressure, passed over between 230—235°/10 mm. Eight grams of the mixed acids were converted into their lead salts, and the latter digested with ether, when the larger portion was dissolved. Both the soluble and insoluble portions were decomposed by hydrochloric acid, and the regenerated fatty acids purified by distillation under diminished pressure. The soluble portion of the lead salts yielded 6 grams of liquid acids, whilst the insoluble portion gave 1·5 grams of solid acids.

The Liquid Acids.—These acids when distilled under diminished pressure passed over between 232° and 235°/15 mm.

An analysis and a determination of the iodine and neutralisation values gave the following results:

0·1366 gave 0·3860 CO_2 and 0·1370 H_2O . C = 77·1; H = 11·1.

0·4095 absorbed 0·8473 iodine. Iodine value = 206·9.

1·1120 neutralised 0·2211 KOH. Neutralisation value = 197·4.

$C_{15}H_{32}O_2$ requires C = 77·1; H = 11·4 per cent. Iodine value = 181·4;
Neutralisation value = 200·4.

$C_{15}H_{30}O_2$ requires C = 77·7; H = 10·8 per cent. Iodine value = 274·1;
Neutralisation value = 201·4.

These results indicated that the liquid acids consisted chiefly of a mixture of linolic and linolenic acids, the former predominating.

The Solid Acids.—These acids were crystallised from glacial acetic acid, but no pure substance could be isolated by this means, the product melting indefinitely between 54° and 58° .

An analysis and a determination of the neutralisation value gave the following results :

0.1432 gave 0.3940 CO_2 and 0.1631 H_2O . C = 75.1 ; H = 12.6.

0.7500 neutralised 0.1559 KOH. Neutralisation value = 207.9.

$\text{C}_{16}\text{H}_{32}\text{O}_2$ requires C = 75.0 ; H = 12.5 per cent. Neutralisation value = 219.1.

$\text{C}_{18}\text{H}_{36}\text{O}_2$ requires C = 76.1 ; H = 12.7 per cent. Neutralisation value = 197.7.

The above results indicated that the solid acids consisted of a mixture of palmitic and stearic acids in about equal proportions.

Ethereal Extract of the Green Resin. Isolation of "Elaterin."

This extract amounted to about 6 grams. A portion of it (about 2 grams) was readily soluble in ether, and consisted of a dark-coloured resin, whilst the remainder (4 grams) was a sparingly soluble, crystalline powder. From the resinous product nothing definite could be isolated, and as it yielded no sugar on boiling with a dilute solution of sulphuric acid in aqueous alcohol, it was not glucosidic.

The above-mentioned, crystalline powder was collected on a filter, washed with ether, and recrystallised from a small volume of absolute alcohol, when it was obtained in small, colourless, hexagonal prisms, melting and decomposing at 210 — 215° . On subjecting this product to fractional crystallisation from absolute alcohol, three principal fractions were obtained. Although a complete separation could not be effected by this means, owing to the limited quantity of material at disposal, the three fractions, nevertheless, exhibited very marked differences, as indicated especially by their solubilities, melting points, and optical rotatory power.

Fraction I.—This fraction formed small, colourless, hexagonal prisms, melting and decomposing at 230° . It was very sparingly soluble in alcohol, and amounted to 0.7 gram :

0.2554, made up to 20 c.c. with chloroform, gave $\alpha_D - 1^{\circ}21'$ in a 2-dcm. tube, whence $[\alpha]_D - 52.4^{\circ}$.

Fraction II.—This fraction closely resembled fraction I in appearance. It was, however, more soluble in alcohol, and melted, with decomposition, at about 210° . It amounted to 1.5 grams.

0.2245, made up to 20 c.c. with chloroform, gave $\alpha_D - 0^{\circ}48'$ in a 2-dcm. tube, whence $[\alpha]_D - 35.6^{\circ}$.

Fraction III.—This fraction crystallised in small, colourless plates,

melting and decomposing at 189—190°. It was very soluble in alcohol, and amounted to only 0.25 gram:

0.2346, made up to 20 c.c. with chloroform, gave $\alpha_D + 0^\circ 24'$ in a 2-dcm. tube, whence $[\alpha]_D + 17.0^\circ$.

The three fractions gave on analysis the following results:

- I. 0.1607 gave 0.4056 CO_2 and 0.1180 H_2O . C = 68.9; H = 8.1.
 II. 0.1468 ,, 0.3710 CO_2 ,, 0.1114 H_2O . C = 68.9; H = 8.4.
 III. 0.1355 ,, 0.3406 CO_2 ,, 0.1005 H_2O . C = 68.6; H = 8.2.
 $\text{C}_{20}\text{H}_{28}\text{O}_5$ requires C = 68.9; H = 8.0 per cent.
 $\text{C}_{24}\text{H}_{34}\text{O}_6$,, C = 68.9; H = 8.0 ,,
 $\text{C}_{28}\text{H}_{38}\text{O}_7$,, C = 69.1; H = 7.8 ,,

From these results it is evident that the above-described, sparingly soluble, crystalline powder corresponds to the product known as "elaterin," and which is recognised under this title by the British and United States Pharmacopœias. The formulæ which have been assigned to elaterin by various investigators are as follows: $\text{C}_{20}\text{H}_{28}\text{O}_5$, Zwenger (*Annalen*, 1842, **43**, 460); $\text{C}_{24}\text{H}_{34}\text{O}_6$, Hemmelmayr (*Ber.*, 1906, **39**, 3380); $\text{C}_{28}\text{H}_{38}\text{O}_7$, Berg (*Bull. Soc. chim.*, 1897, [iii], **17**, 85; 1906, [iii], **35**, 435). It has, however, quite recently been shown by the present authors (*Pharm. J.*, 1909, [iv], **29**, 501) that the product known as elaterin is not homogeneous, as has hitherto been assumed, but that it consists of a mixture of substances which, although possessing apparently the same percentage composition, differ essentially in their physical properties, especially in their optical rotatory power, as also in their physiological action. The above-noted results of the present investigation therefore afford further confirmation of the previous conclusions.

The final alcoholic mother liquors obtained during the separation of the above-described elaterin fractions yielded, on dilution with water, a small amount of a colourless substance, which crystallised in small needles and melted and decomposed at 168—170°:

0.2098, heated at 115°, lost 0.0070 H_2O . $\text{H}_2\text{O} = 3.3$.

0.1318 of anhydrous substance gave 0.3264 CO_2 and 0.0980 H_2O . C = 67.5; H = 8.2.

A determination of its specific rotatory power gave the following result:

0.2942 of anhydrous substance, made up to 20 c.c. with chloroform, gave $\alpha_D + 0^\circ 38'$ in a 2-dcm. tube, whence $[\alpha]_D + 21.5^\circ$.

These results would indicate that the above-described substance consisted to a considerable extent of the dextrorotatory constituent of elaterin, but the amount of material available was so small that it was impossible to obtain any evidence of its purity.

Inasmuch as we have shown that the product known as elaterin consists of two substances of apparently the same percentage composition, one of which is levorotatory and devoid of physiological activity, whilst the other is dextrorotatory and possesses an intensely purgative action, it seems desirable that the respective substances should be designated by distinctive names. It is therefore proposed to designate the chief constituent of crude elaterin, which is levorotatory, as α -elaterin, and the dextrorotatory, physiologically active constituent, as β -elaterin.

Chloroform and Alcohol Extracts of the Green Resin.

Both of these extracts consisted of brown, resinous material, and they amounted to 0.3 and 0.5 gram respectively. As nothing definite could be isolated from them, they were united, and boiled for some hours with a dilute solution of sulphuric acid in aqueous alcohol. No sugar was formed by this treatment, and the extracts, therefore, were evidently not glucosidic.

Examination of the Brown Resin (B).

This was a light brown powder, and amounted to 6.5 grams. It was dissolved in alcohol, and mixed with purified sawdust, the thoroughly dried mixture being then successively extracted in a Soxhlet apparatus with ether, chloroform, and alcohol. The ether removed about 5.5 grams of material, from which, with the exception of small amounts of elaterin, nothing definite could be isolated. The chloroform and alcohol extracts amounted to only 0.2 and 0.5 gram respectively, and consisted of brown resins. Nothing of a glucosidic nature was contained in any of these extracts.

Examination of the Aqueous Liquid (C).

This liquid, as already indicated, represented that portion of the original alcoholic extract of the *Ecballium* fruits which was soluble in cold water, and from which the previously-described resins (A) and (B) had been separated. It was extracted many times with ether, the combined ethereal liquids being washed, dried, and the solvent removed, but only a small amount of an indefinite, amorphous product was thus obtained.

The aqueous liquid, after extraction with ether, was shaken with successive portions of amyl alcohol, the combined extracts being washed, and the solvent removed by distillation under diminished pressure. A quantity (about 15 grams) of resinous material was thus obtained, which was only sparingly soluble in water. As nothing

definite could be isolated from it, it was boiled for some hours with dilute alcohol containing 3 per cent. of its weight of sulphuric acid. The chief product of this operation was, however, entirely resinous, and, as no sugar was formed, it was evident that the material contained nothing glucosidic.

After extraction with amyl alcohol, as above described, the aqueous liquid was concentrated, and treated with a large volume of strong alcohol. This precipitated a quantity of inorganic material, consisting chiefly of potassium chloride and sulphate, together with a sugar which yielded *d*-phenylglucosazone, melting at 216°. The clear liquid was then decanted and the alcohol removed, when a small quantity of a syrup was obtained. This was dissolved in a small quantity of water and kept for several days, but nothing separated. The solution was then diluted with water, and, after adding 5 per cent. of its weight of sulphuric acid, the whole was boiled for several hours. The only products resulting from this treatment that could be identified were a little formic acid and furfuraldehyde.

Summary.

The results of the present investigation of the fruit of *Ecballium Elaterium* may be summarised as follows:

In accordance with the previous observation of Berg (*Bull. Soc. chim.*, 1897, [iii], 17, 85), the fruit was found to contain a small amount of an enzyme which is capable of hydrolysing β -glucosides.

The liquid obtained by the extraction of 27 kilograms of the fresh fruit with alcohol yielded, on concentration, a quantity (45.5 grams) of a green resin, and, by the further evaporation of the liquid, 6.5 grams of brown, resinous material were separated. The green resin, when extracted with various solvents, yielded a very small amount of a hydrocarbon (m. p. 68°), which was probably hentriacontane, $C_{31}H_{64}$; a phytosterol, $C_{27}H_{46}O$ (m. p. 148°; $[\alpha]_D + 3.2^\circ$); a substance melting at 258—260°, which appears to be related to ipuranol, $C_{23}H_{38}O_2(OH)_2$; a mixture of fatty acids; and a product corresponding to the so-called "elaterin," the characters of which have previously been elucidated by the authors (*Pharm. J.*, 1909, [iv], 29, 501). It is now proposed to designate the levorotatory constituent of crude elaterin as α -elaterin, and the dextrorotatory, physiologically active constituent as β -elaterin. From the brown, resinous material, with the exception of small amounts of elaterin, nothing definite could be isolated. The portion of the alcoholic extract of the fruit which was soluble in water contained a considerable amount of inorganic salts, consisting chiefly of potassium chloride and sulphate, and a sugar which yielded *d*-phenylglucosazone (m. p. 216°).

No evidence could be obtained of the presence of a glucoside of elaterin, which has been stated by Berg (*loc. cit.*) to be contained in the juice of the fresh fruit, nor could any other glucosidic substance be detected. It was, on the other hand, quite definitely ascertained that the so-called "elaterin" exists in the fruit as such and not in a combined state. The various amorphous products which were described many years ago by Walz (*N. Jahrb. Pharm.*, 1859, **11**, 21, 178) under the names of prophetin, ecbalin or elateric acid, hydroelaterin, and elateride were evidently indefinite mixtures, and are therefore entitled to no further consideration in chemical literature.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C.

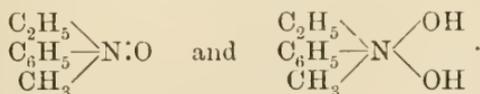
CCXIX.—*The Resolution of Asymmetrical Derivatives of Phosphoric Acid.*

By BERNARD DUNSTAN WILKINSON LUFF (1851 Exhibition Scholar)
and FREDERIC STANLEY KIPPING.

IN the case of all the optically active compounds which are known at the present time, with the exception of methylcyclohexylideneacetic acid (Perkin, Pope, and Wallach, this vol., p. 1789), and possibly with the further exception referred to below, the optical activity is due to the presence of one or more fully saturated asymmetric groups. To the best of our knowledge there is no recorded instance in which optical activity is conditioned by the presence in the molecule of an unsaturated asymmetric complex, such as one of those represented by the following symbols:



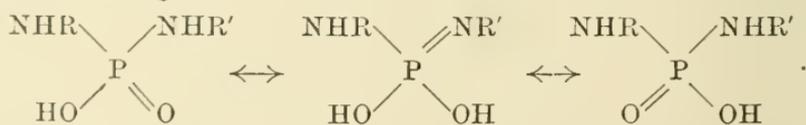
The possible exception is that afforded by the work of Meisenheimer, who has shown (*Ber.*, 1908, **41**, 3966) that methylethylaniline oxide may be resolved into enantiomorphously related components, which are optically active in solution. But, as Meisenheimer himself points out, the base in solution may be either the oxide or the hydroxide, represented respectively by the formulæ:



Consequently, as it is not yet known which of these forms is actually present, the possible existence of optically active compounds of the unsaturated type indicated above is left an open question. Long before the publication of Meisenheimer's results, attempts were made in these laboratories to prepare an unsaturated asymmetric phosphorus compound of the type $\text{POR}_1\text{R}_2\text{R}_3$, and then to resolve it into its optically active components. The first of these tasks was, in fact, successfully accomplished several years ago by Caven (Trans., 1902, **81**, 1362), who obtained anilino-*p*-toluidinophosphoric acid, $\text{PO}(\text{NHPh})(\text{NH}\cdot\text{C}_6\text{H}_4\text{Me})\cdot\text{OH}$, methoxy-*p*-toluidinophosphoric acid, $\text{PO}(\text{NH}\cdot\text{C}_6\text{H}_4\text{Me})(\text{OMe})\cdot\text{OH}$, and other asymmetric compounds from phosphoryl chloride; on the other hand, the few experiments on the resolution of these acids which were made at that time on a very small scale by one of us gave only negative results.

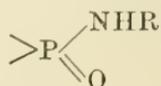
As the further investigation of this matter seemed to be of some importance, anilino-*p*-toluidinophosphoric acid was prepared by the method described by Caven (*loc. cit.*), and its cinchonidine, strychnine, and quinine salts were submitted to fractional crystallisation; in all three cases negative results only were obtained. The experiments with salts of this acid, however, were not continued beyond this stage, firstly because of the relative instability of the acid, and secondly because, as already pointed out by Caven (*loc. cit.*), there is, theoretically, a possibility of the occurrence of tautomeric or isodynamic change in the molecule of an acid of this type, whether it is in the free state or in combination with a base.

In the case of the acid, the hydroxylic hydrogen atom might simply wander from one oxygen atom to the other, or a similar end result might be reached by the more complex changes indicated in the following scheme:



If either of these processes occurred, the existence of an optically active acid of this type in the free state would, of course, be impossible.

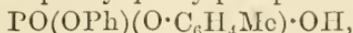
In the case of the salts of the acid, even assuming that hydrolysis did not occur, intramolecular change in the grouping



might still take place. As a result of such a molecular rearrange-

ment, it is not inconceivable that on crystallising a salt of anilino-*p*-toluidinophosphoric acid which contained an active base, all the acid molecules might be transformed into *one* of the optically active forms, namely, that which gave the more sparingly soluble salt. A resolution or transformation of this character, provided that it occurred sufficiently rapidly, would not be detected unless the specific rotation of the salt in aqueous solution could be determined, and the observed behaviour of the salt would simulate that of a non-resolvable partially racemic substance. In view of these possibilities, it seemed better to prepare some asymmetric substituted phosphoric acid in which the possibility of tautomeric or isodynamic change was excluded, or, at any rate, was very remote. Consequently, attempts were made to obtain methoxymethylanilino-phosphoric acid and ethoxymethylanilinophosphoric acid, but without success.

The preparation of phenyl-*p*-tolylphosphoric acid,



was then undertaken, and was accomplished without difficulty by treating phenylphosphoryl chloride with sodium *p*-tolyl oxide and decomposing the phenyl-*p*-tolylphosphoryl chloride with water. This acid, in the form of its salts, is fairly stable towards water, and in the hope of resolving it into its optically active components many of its salts containing an active base were submitted to fractional crystallisation from various solvents; after systematic treatment, the extreme fractions were collected, and their melting points were determined as well as their specific rotations in methyl-alcoholic solution.*

The following table contains a summary of the results thus obtained:

Salts of Phenyl-p-tolylphosphoric Acid, PO(OPh)(O·C₆H₄Me)·OH.

Salt.	"Most sparingly soluble" fraction.		"Least sparingly soluble" fraction.	
	M. p.	$[\alpha]_D$.	M. p.	$[\alpha]_D$.
Cinchonidine	195—196°	-77·3°	194—195°	-75·0°
Quinine	170	-120·6	163—169	-121·1
<i>l</i> -Menthylamine	198—200	-16·0	198—200	-15·4
Strychnine	149—150	-10·1	149—150	-11·2
Brucine.....	168—169	-6·1	167—168	-6·4
Cinchonine	194—195	+120·9	194—195	+121·3
<i>d</i> -Methylhydrindamine	135—137	+16·9	132—134	+16·5
<i>d</i> -Hydrindamine	128—129	—	128—129	—

It will be seen from these data that in no case was there any evidence whatever of a resolution having occurred; all the fractions

* All the specific rotations given in this paper were determined in 98 per cent. methyl-alcoholic solution.

of a given compound appeared to be homogeneous, and were identical in melting point and specific rotation within the limits of experimental error.

Now there seem to be no reasonable grounds for attributing these negative results to the occurrence of tautomeric or isodynamic change. It is not impossible, of course, that in aqueous and related solvents the salts may be partially hydrolysed, and that the free acid may then undergo isomeric change; if this were so the consequences might be similar to those discussed in the case of the amino-acids, that is to say, the whole of the deposited salt might be derived from one of the active acids without there being any evidence that such was the fact. But fractional crystallisation of some of the above salts from ethyl acetate, ether, and other non-hydrolysing liquids gives the same negative result as that obtained with the use of aqueous alcohol; hydrolysis, followed by intramolecular change in the acid, seems therefore to be excluded as a possible explanation of the observations.

It has been shown by Kipping and Hall (Trans., 1901, **79**, 444) that, in accordance with theoretical considerations, an externally compensated acid chloride, such as *dl*-phenylchloroacetyl chloride, gives, with an externally compensated base, such as *dl*-hydrindamine, two isomeric amides; these isomerides are themselves externally compensated, and if A represents the acid, and B the basic nucleus, the one is a mixture or racemic compound of *dBdA* and *lBlA*, the other a mixture or racemic compound of *dBlA* and *lBdA*.

As the result of the examination of many salts of phenyl-*p*-tolylphosphoric acid failed to give any indication of the asymmetry of the acid molecule, it seemed advisable, before going further, to obtain, if possible, some evidence of this asymmetry by the application of the method just described.

For this purpose, phenyl-*p*-tolylphosphoryl chloride was treated with *dl*-hydrindamine in ethereal solution, and the product was examined. Its whole behaviour showed at once that it was a mixture; it could hardly be recrystallised without this fact becoming noticeable, and from it, in the first place, a crystalline compound melting at 98—100° was isolated without very much difficulty. After protracted crystallisation, there was obtained a second compound, melting at 85—87°, but which was doubtless not quite free from the substance of higher melting point. Analyses and a careful examination of these two products showed that they were isomeric hydrindamides of the formula $\text{PO}(\text{OPh})(\text{O}\cdot\text{C}_6\text{H}_4\text{Me})\cdot\text{NH}\cdot\text{C}_9\text{H}_9$; and that the compound of lower melting point was, in fact, a distinct substance, and not merely

an impure form of the amide of higher melting point, was conclusively established.

The result of the experiment made with *dl*-hydrindamine rendered it probable that the acid was a mixture of enantiomorphously related isomerides, and that, by employing one of the active bases, these isomerides, in the form of their hydrindamides, might be separated from one another. Such a resolution would be strictly comparable to that which may be brought about by fractionally crystallising the amide formed from a *dl*-base and an optically active acid (Kipping and Salway, *Trans.*, 1904, **85**, 438).

The *d*-hydrindamide of phenyl-*p*-tolylphosphoric acid, therefore, was prepared; in this case, also, the product was obviously a mixture, and when fractionally crystallised it yielded two isomeric substances.

The more sparingly soluble or α -compound melted at 127° , and had $[\alpha]_D - 17.4^{\circ}$; the β -isomeride, which no doubt contained some of the α -compound, melted at $82-86^{\circ}$, and had $[\alpha]_D - 21.2^{\circ}$. Although the difference in value between the specific rotations of the two isomerides is not large, the fact that the more readily soluble β -compound has the higher rotation is important evidence that the latter is not simply the impure α -derivative, the absence of *d*-hydrindamine salt in the samples having, of course, been proved very carefully.

As a confirmatory experiment, the *l*-menthylamide of the acid was prepared, and the product was submitted to fractional crystallisation. Here again the more sparingly soluble or α -isomeride was separated in a pure state without any great difficulty; it melted at 110° , and had $[\alpha]_D - 32.3^{\circ}$. The β -isomeride, obtained from the mother liquors, and probably not quite free from the α -compound, melted at $85-86^{\circ}$, and had $[\alpha]_D - 37.9^{\circ}$.

The fact that the acid is so easily resolved into two compounds by the fractional crystallisation of the amides which it forms with active bases is in strange contrast to the behaviour which it shows when it is combined as the salt of an active base. On comparing the structures of the two classes of compounds, it would seem that isomeric change of a recognised common type might occur much

more easily in the case of the amides, $\text{>P} \begin{array}{l} \text{NHR} \\ \text{O} \end{array}$, than in that of

the salts, $\text{>P} \begin{array}{l} \text{O} \cdot \text{NH}_3\text{R} \\ \text{O} \end{array}$.

But, since the amides are quite stable and may be repeatedly crystallised without their undergoing any alteration in properties,

it seems reasonable to conclude that the occurrence of intramolecular rearrangement has nothing to do with the failure to resolve the acid by crystallising its salts with active bases.

From the results of this investigation, it also seems clear that phenyl-*p*-tolylphosphoric acid is a mixture of enantiomorphously related isomerides, and that the unsaturated grouping (I) is comparable with the saturated complex (II):



Unfortunately, although the optically active components of the acid have in all probably been separated from one another, their preparation in the free state was not practicable, owing to the stability of the amides in which they were contained.

EXPERIMENTAL.

Anilino-*p*-toluidinophosphoric acid,



was prepared by the method described by Caven (*Trans.*, 1902, **81**, 1369), and was purified by dissolving it in 50 per cent. alcohol containing ammonia, and then acidifying the solution with hydrochloric acid. The compound is thus obtained in pearly leaflets, and there is less decomposition than when aqueous alcohol or acetone alone is employed as solvent.

*Strychnine Anilino-*p*-toluidinophosphate.*

This salt was precipitated in crystals on adding a solution of strychnine hydrochloride to a solution of the ammonium salt of the acid. It was washed with water and fractionally crystallised from cold aqueous methyl alcohol, from which solvent it was deposited in glistening needles. After about twelve crystallisations, extreme fractions were examined; the specific rotations were determined in methyl-alcoholic solution.*

“*Most sparingly soluble*” fraction.—M. p. 137—138°. 1.349 (dried at 100°), made up to 25 c.c., gave, in a 2-dcm. tube, $\alpha - 0.71^\circ$, whence $[\alpha]_D - 7.3^\circ$.

“*Least sparingly soluble*” fraction.—M. p. 137—138°. 0.69 (dried at 100°), made up to 20 c.c., gave, in a 2-dcm. tube, $\alpha - 0.49^\circ$, whence $[\alpha]_D - 7.1^\circ$.

The salt crystallises from aqueous solvents in prismatic needles,

* See footnote on p. 1995.

and is readily soluble in acetone, chloroform, and the common alcohols, but is only sparingly soluble in benzene and almost insoluble in light petroleum. On repeatedly crystallising the salt from aqueous alcohol, slight decomposition occurred, so that the final mother liquors, which were brown and had an odour of *p*-toluidine, were discarded in the above operations.

Cinchonidine Anilino-p-toluidinophosphate.

This compound was obtained as a crystalline precipitate on the addition of cinchonidine hydrochloride to a solution of the ammonium salt; after one crystallisation from aqueous methyl alcohol, it melted at 203°, but after one or two more recrystallisations the melting point fell to 199°. This was due to hydrolysis brought about by the prolonged heating with the solvent which was necessary to redissolve the salt.

As the compound was insoluble in non-hydrolysing solvents such as benzene, its investigation was not continued.

Quinine Anilino-p-toluidinophosphate.

This salt was precipitated as a solid on adding a solution of quinine hydrochloride to a solution of the ammonium salt of the acid. It was washed and dried, and dissolved in a mixture of hot benzene and light petroleum containing a little methyl alcohol; from this mixture it was deposited in crystals melting at 155—156°, but after it had been separated into several fractions as the result of three or four similar recrystallisations, the melting point ranged from 160° to 175°; this result seemed to be due to the employment of a larger proportion of methyl alcohol in the solvent, for, when these fractions were recrystallised from benzene and petroleum containing only a trace of methyl alcohol, the melting point fell again to 155—156°. It was also found that when the solid melting at 155—156° was warmed on the water-bath with benzene, the melting point gradually rose to 180—181°; the same result was obtained by crystallising a portion of the salt melting at 155—156° from aqueous methyl alcohol, the lustrous prisms thus obtained melting at 180—181°. A mixture of the samples melting at 155—156° and 180—181° respectively liquefied at about 175°. Further, on dissolving some of the salt melting at 180—181° in cold chloroform, and then adding light petroleum, there was precipitated an oil which set to a glassy solid; the latter, when heated slowly, swelled up to a frothy mass at 80—100°, and seemed to melt at about 130°, properties which it retained even when kept during some days.

It seems from these observations that the quinine salt exists in three modifications, which are easily converted one into the other by recrystallisation, but the matter was not further investigated.

Determinations of the specific rotations of the samples melting at 180—181° and 155—156° respectively confirmed the conclusion that the different melting points observed were not due to a resolution of the acid having occurred:

Salt melting at 180—181°.—0·7398, made up to 25 c.c., gave, in a 2-dcm. tube, $\alpha - 7\cdot76^\circ$, whence $[\alpha]_D - 131\cdot0^\circ$.

Salt melting at 155—156°.—0·7114, under the same conditions, gave $\alpha - 7\cdot39^\circ$, whence $[\alpha]_D - 129\cdot8^\circ$.

Experiments on the Preparation of an Alkylloxymethylanilino-phosphoryl Chloride.

An attempt was made to prepare methoxymethylanilinophosphoryl chloride, $\text{PO}(\text{OMe})(\text{NMePh})\text{Cl}$, by treating methoxyphosphoryl chloride (1 mol.) with methylaniline (2 mols.) in benzene solution; no immediate precipitation of methylaniline hydrochloride occurred, but in the course of half an hour crystals began to separate. After the mixture had remained overnight, the solution was filtered and evaporated, when a viscid, oily liquid remained. Similar experiments, using ether or light petroleum as solvent, gave similar results, but it was found to be impossible to isolate any crystalline substance from the crude oily product; attempts to prepare the corresponding ethoxy-derivative were also unsuccessful.

Phenyl-p-tolylphosphoryl Chloride, $\text{PO}(\text{OPh})(\text{O}\cdot\text{C}_6\text{H}_4\text{Me})\text{Cl}$.

A thin paste of sodium *p*-tolylxide (1 mol.) and ether, prepared by treating an ethereal solution of *p*-cresol with sodium wire, was slowly run into an ethereal solution of phenylphosphoryl chloride (1 mol.), the whole being well stirred during the operation. The reaction took place immediately, sodium chloride being deposited in a microcrystalline form. After some time the solution was filtered in absence of moisture; the ether was then evaporated, and the residue submitted to fractional distillation under 35 mm. pressure. Fractions were first collected boiling at (I.) below 235°, (II) 235—255°, and (III) 255—275°, and during this first distillation sodium chloride separated in moderate amount. After further systematic operations, a large proportion of liquid boiling at 244—248°/35 mm. was obtained.

An analysis of this fraction gave the following result:

0·643 gave 0·317 AgCl. $\text{Cl} = 12\cdot1$.

$\text{C}_{13}\text{H}_{12}\text{O}_3\text{ClP}$ requires $\text{Cl} = 12\cdot5$ per cent.

Phenyl-p-tolylphosphoryl chloride is a colourless, highly refractive liquid, which does not fume in moist air until it has been exposed for some time; it is only slowly acted on by cold water, giving the corresponding acid, but it is readily converted into the sodium salt of the acid when it is warmed with dilute sodium hydroxide solution.

Phenyl-p-tolylphosphoric Acid, $\text{PO}(\text{OPh})(\text{O}\cdot\text{C}_6\text{H}_4\text{Me})\cdot\text{OH}$.

The chloride was placed in a stoppered bottle with an excess of 10 per cent. sodium hydroxide solution, and the contents were then warmed to about 60° and shaken vigorously. In a short time the chloride passed into solution, and, on acidifying, an oil was deposited; the supernatant liquid was then decanted, and the oil, after having been washed with water, was dried over sulphuric acid. In the course of a few days it solidified, and was then purified by crystallisation from a mixture of benzene and light petroleum; the acid was thus obtained in tufts of radiated, wax-like needles, melting at 54° . On analysis:

0.1706 gave 0.3692 CO_2 and 0.0772 H_2O . $\text{C}=59.0$; $\text{H}=5.0$.

$\text{C}_{13}\text{H}_{13}\text{O}_4\text{P}$ requires $\text{C}=59.1$; $\text{H}=4.9$ per cent.

The equivalent of the acid was determined by means of standard barium hydroxide solution; this gave a value of 262, the calculated equivalent of phenyl-*p*-tolylphosphoric acid being 264.

The acid is nearly insoluble in water and in light petroleum, but is soluble in chloroform, benzene, and the common alcohols; it is not readily hydrolysed by alkalis, prolonged boiling being necessary. In subsequent preparations of the acid, the pure chloride was not isolated, but the crude product obtained by the interaction of the phenylphosphoryl chloride and sodium *p*-tolyl-oxide, after evaporating the ether, was treated as follows.

The residue was washed into a stoppered bottle with 10 per cent. sodium hydroxide solution, and the mixture warmed to about 60° ; the whole was then violently shaken, and after a few minutes the oil had almost completely passed into solution, only a small proportion remaining undissolved. As the liquid cooled, this insoluble oil solidified, and was then separated; it is described later.

The clear alkaline solution was treated with excess of hydrochloric acid, whereupon the phenyl-*p*-tolylphosphoric acid was precipitated as an oil; after having been washed and dried in a vacuum desiccator, it solidified to a crystalline mass, melting at 53° .

Phenyl Di-p-tolyl Phosphate, $\text{PO}(\text{O}\cdot\text{C}_6\text{H}_4\text{Me})_2\cdot\text{OPh}$.

This compound was formed in small quantities in the preparation of phenyl-*p*-tolylphosphoryl chloride, and remained as a solid when samples of the impure chloride were treated in the manner just described; after crystallisation from light petroleum, it melted at 54° . An estimation of phosphorus was carried out by igniting a mixture of the solid and sodium peroxide, and subsequently titrating with standard uranium nitrate:

0.584 required 23.6 c.c. uranium nitrate (1 c.c. = 0.00209 gram P).

P = 8.4.

$\text{C}_{20}\text{H}_{19}\text{O}_4\text{P}$ requires P = 8.7 per cent.

The ester is soluble in the common alcohols, benzene, and light petroleum, and crystallises in rectangular plates.

Cinchonidine Phenyl p-Tolyl Phosphate.

On the addition of cinchonidine hydrochloride to a solution of the ammonium salt of the acid, a white, crystalline precipitate was immediately obtained. The salt was separated by filtration, washed, and fractionally crystallised from hot aqueous alcohol, from which solvent it was deposited in long, silky needles. After about eight recrystallisations, the extreme fractions were examined:

"*Most sparingly soluble*" fraction.—M. p. $195-196^\circ$. 0.291 (dried at 100°), made up to 25 c.c., gave, in a 2-dcm. tube, $\alpha - 1.80^\circ$, whence $[\alpha]_D - 77.3^\circ$.

"*Least sparingly soluble*" fraction.—M. p. $194-195^\circ$. 0.237, under the same conditions, gave $\alpha - 1.42^\circ$, whence $[\alpha]_D - 75.0^\circ$.

The salt is soluble in cold ethyl acetate, chloroform, acetone, and the common alcohols, but is insoluble in light petroleum. A sample of the salt was also fractionally crystallised from a hot mixture of benzene and light petroleum, but the extreme fractions had the same properties as when aqueous alcohol was used.

Quinine Phenyl p-Tolyl Phosphate.

This salt was precipitated as an oil on adding a solution of quinine hydrochloride to a solution of the ammonium salt, but it soon solidified. A sample was fractionally crystallised from aqueous alcohol, from which it separated in a somewhat flocculent form; extreme fractions obtained after about eight recrystallisations had the same melting points and the same specific rotations.

"*Most sparingly soluble*" fraction.—M. p. 170° . 0.2446, made up to 25 c.c., gave, in a 2-dcm. tube, $\alpha - 2.36^\circ$, whence $[\alpha]_D - 120.6^\circ$.

"Least sparingly soluble" fraction.—M. p. 168—169°. 0.383, under the same conditions, gave $\alpha - 3.77^\circ$, whence $[\alpha]_D - 121.1^\circ$.

The quinine salt is deposited from both aqueous and dry solvents in felted masses of microscopic needles; it is soluble in cold ethyl acetate, chloroform, and the common solvents, but is insoluble in light petroleum. A sample of salt fractionally crystallised from a mixture of chloroform and light petroleum gave the same results as those obtained by employing aqueous alcohol as solvent.

l-Menthylamine Phenyl p-Tolyl Phosphate.

The oily salt, prepared by precipitation, did not solidify for some time. It was washed with water and fractionally crystallised from aqueous alcohol at the ordinary temperature, the process being continued until the "most sparingly soluble" portion had been crystallised eight times. The two extreme fractions were then examined, but the results showed that a resolution had not occurred:

"Most sparingly soluble" fraction.—M. p. 198—200°. 0.1064, made up to 20 c.c., gave, in a 2-dcm. tube, $\alpha - 0.17^\circ$, whence $[\alpha]_D - 16.0^\circ$.

"Least sparingly soluble" fraction.—M. p. 198—200°. 0.1426, under the same conditions, gave $\alpha - 0.22^\circ$, whence $[\alpha]_D - 15.4^\circ$.

The salt crystallises from aqueous alcohol in long, silky needles; it is soluble in nearly all organic solvents, such as benzene, light petroleum, and ethyl acetate, even in the cold.

Strychnine Phenyl p-Tolyl Phosphate.

This salt was systematically crystallised from aqueous alcohol at the ordinary temperature, and extreme fractions were then examined:

"Most sparingly soluble" fraction.—M. p. 150—151°. 0.335, made up to 20 c.c., gave, in a 2-dcm. tube, $\alpha - 0.34^\circ$, whence $[\alpha]_D - 10.1^\circ$.

"Least sparingly soluble" fraction.—M. p. 150—151°. 0.338, under the same conditions, gave $\alpha - 0.34^\circ$, whence $[\alpha]_D - 11.2^\circ$.

The salt crystallises from aqueous solvents in rosettes of needles, and is soluble in acetone, chloroform, or alcohol, but is insoluble in light petroleum.

Brucine Phenyl p-Tolyl Phosphate.

On adding brucine hydrochloride solution to a solution of the ammonium salt, an oil was first precipitated, which redissolved on

stirring; on further addition of the hydrochloride, however, a permanent, oily precipitate was obtained. The salt did not solidify, even in the course of some days, but when washed with water and evaporated with methyl alcohol it was obtained as a glassy mass. The compound could not be obtained in crystals from aqueous solvents, but from hot ethyl acetate, containing a little methyl alcohol, it separated in prisms; it was fractionally crystallised from this mixture about eight times, and extreme fractions were then examined:

"*Most sparingly soluble*" fraction.—M. p. 168—169°. 0.821, made up to 20 c.c., gave, in a 2-dcm. tube, $\alpha - 0.50^\circ$, whence $[\alpha]_D - 6.1^\circ$.

"*Least sparingly soluble*" fraction.—M. p. 167—168°. 0.894, under the same conditions, gave $\alpha - 0.58^\circ$, whence $[\alpha]_D - 6.4^\circ$.

The brucine salt was obtained in another crystalline form by keeping the oily precipitate for some weeks; at the end of this time it began to solidify, giving well-defined prisms. These contained water of crystallisation, and, when anhydrous, melted at 116—118°; on recrystallisation from ethyl acetate and methyl alcohol, however, the compound melting at 168—169° was deposited.

The salt is soluble in chloroform, acetone, and the common alcohols, but is insoluble in light petroleum, ethyl acetate, or benzene.

Cinchonine Phenyl p-Tolyl Phosphate.

This salt remained oily during several hours, but after having once solidified it crystallised readily from weak aqueous alcohol. It was fractionally crystallised from this solvent, and after ten operations extreme fractions were collected and examined:

"*Most sparingly soluble*" fraction.—M. p. 194—195°. 0.214, made up to 25 c.c., gave, in a 2-dcm. tube, $\alpha + 2.07^\circ$, whence $[\alpha]_D + 120.9^\circ$.

"*Least sparingly soluble*" fraction.—M. p. 193—194°. 0.164, under the same conditions, gave $\alpha + 1.99^\circ$, whence $[\alpha]_D + 121.3^\circ$.

The cinchonine salt crystallises in prismatic needles, and is soluble in cold chloroform, acetone, benzene, and the common alcohols, but is insoluble in light petroleum.

d-Methylhydrindamine Phenyl p-Tolyl Phosphate.

The *d*-methylhydrindamine salt of phenyl-*p*-tolylphosphoric acid was prepared by fractionally precipitating a solution of the sodium salt with the hydrochloride of the *d*-base. The first separation did not solidify for some time, but all later fractions, which were only

precipitated after the first one had crystallised, solidified immediately. Three main fractions were thus obtained; they all melted at 123—125° after having been recrystallised once from aqueous methyl alcohol.

As fractional precipitation from aqueous solvents had given negative results, the whole of the salt was washed and dried and systematically crystallised from a mixture of ethyl acetate and ether. The most sparingly soluble portion thus obtained, after about six operations, melted at 135—137°, the most readily soluble one at 132—134°, but the two preparations gave the same specific rotations:

“*Most sparingly soluble*” fraction.—M. p. 135—137°. 0·467, made up to 20 c.c., gave, in a 2-dcm. tube, $\alpha + 0\cdot79^\circ$, whence $[\alpha]_D + 16\cdot9^\circ$.

“*Least sparingly soluble*” fraction.—M. p. 132—134°. 0·836, under the same conditions, gave $\alpha + 1\cdot34^\circ$, whence $[\alpha]_D + 16\cdot5^\circ$.

The whole of the salt was then fractionally crystallised from anhydrous acetone about six times; the most sparingly soluble fraction melted at 135—137°, and when examined polarimetrically gave the following result:

0·887, made up to 20 c.c., gave, in a 2-dcm. tube, $\alpha + 1\cdot49^\circ$, whence $[\alpha]_D + 16\cdot8^\circ$.

The further examination of this salt showed that the different melting points of preparations from aqueous methyl alcohol and from ethyl acetate or acetone were not due to a resolution of the acid having occurred; although many experiments were made, the conditions leading to the production of the different crystalline forms were not very satisfactorily established. Sometimes the crystals obtained from a mixture of ethyl acetate and ether melted at 124—125°; sometimes they only sintered at this temperature very slightly and then melted at 134—136°; occasionally they only showed faint signs of sintering at 125°, and partially and suddenly melted at 130—131°, the rest liquefying at 135—136°.

The salt is very readily soluble in methyl alcohol, and dissolves freely in hot ethyl acetate or hot acetone, but it is only sparingly soluble in ether, and practically insoluble in cold water.

d-Hydrindamine Phenyl p-Tolyl Phosphate.

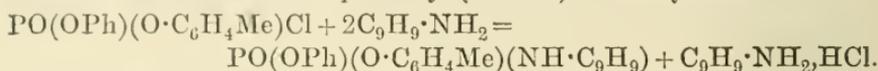
This salt was prepared from the sodium salt by precipitation, but not in large quantities; it remained oily during several hours, but after having solidified it crystallised well from aqueous methyl alcohol in colourless prisms, melting at 128—129°. Fractional crystallisation from the solvent just named, and also from a mixture

of ethyl acetate and ether, failed to give any sign of resolution; the melting point of the salt obtained from ethereal solutions seemed to be 3° lower than that of preparations from aqueous solvents—an indication of dimorphism, which was not further examined.

The salt is soluble in methyl alcohol and hot ethyl acetate, but only sparingly soluble in cold ether and in cold water.

Isomeric dl-Hydrindamides of Phenyl-p-tolylphosphoric Acid.

These compounds were prepared by the interaction in ethereal solution of phenyl-*p*-tolylphosphoryl chloride (1 mol.) and a slight excess of the theoretical quantity (2 mols.) of *dl*-hydrindamine:



An immediate precipitate of *dl*-hydrindamine hydrochloride was formed, and the reaction seemed to be at an end almost immediately, but to ensure its completion the solution was left for twelve hours at the ordinary temperature. The hydrochloride of the base was then separated by filtration, and the ethereal solution was evaporated at the ordinary temperature; the residue, a crystalline solid mixed with oil, was washed with very dilute acetic acid, and then fractionally crystallised from aqueous methyl alcohol.

α -Isomeride.—After a great many operations the substance most sparingly soluble in methyl alcohol was obtained in fairly well-defined, transparent prisms; it was dried over sulphuric acid until constant, and analysed, with the following result:

0.1675 gave 0.4291 CO_2 and 0.0902 H_2O . C = 69.86; H = 5.9.

$\text{C}_{22}\text{H}_{22}\text{O}_3\text{NP}$ requires C = 69.65; H = 5.8 per cent.

This *dl*-hydrindamide melts at 98 — 100° , and solidifies, on cooling, to a crystalline mass, which does not melt until 104 — 105° , although it sinters at lower temperatures. These observations seem to show that this *α* -isomeride is dimorphous, and on at least two occasions during its purification it separated from aqueous methyl alcohol in crystals which melted at 105° , but the exact conditions required for the production of this modification were not determined.

The compound is very readily soluble in methyl alcohol, chloroform, or ethyl acetate, and slightly soluble in boiling ether, but only very sparingly soluble in boiling light petroleum, and practically insoluble in cold water.

β -Isomeride.—After having separated all the more sparingly soluble portions (which consisted mainly of the *α* -isomeride), there remained eight or ten fractions, which had been obtained by systematically crystallising the mixture of hydrindamides from methyl alcohol; the most sparingly soluble portion melted at about

94°, the most readily soluble one at 74°, the intermediate ones at temperatures between these extremes in regular gradation. The several portions were next systematically extracted with cold ether, and all the more soluble material was then collected and fractionally crystallised from a mixture of ether and light petroleum; in this way there was obtained, as the most sparingly soluble portion, a preparation, obviously not quite pure, which sintered at about 72°, melting completely at 74—76°. This sample was dried and analysed:

0·1758 gave 0·4485 CO₂ and 0·0951 H₂O. C = 69·57; H = 6·0.

C₂₂H₂₂O₃NP requires C = 69·65; H = 5·8 per cent. —

As this result seemed to prove the existence of a hydrindamide isomeric with the compound described above, the impure preparation melting at 74—76° was fractionally crystallised from aqueous methyl alcohol, and at last a small proportion of it was obtained in long, colourless needles, melting at 85—87°. On analysis:

0·1741 gave 0·4466 CO₂ and 0·0930 H₂O. C = 69·96; H = 5·9.

That the substance melting at 85—87° is not merely an impure form of the α -isomeride was proved by mixing it with an approximately equal proportion of the latter; the mixture sintered at 75°, and was completely melted at 83°.

These two hydrindamines are so very similar in appearance and in properties that their separation is only accomplished with very great difficulty, a fact which is perhaps strong confirmatory evidence of their isomerism. That the two substances are amides, and not salts, is proved, not only by the analytical results, but also by the fact that they are not appreciably changed by sodium carbonate in aqueous alcoholic solution; in fact, they can be warmed in contact with aqueous sodium hydroxide for some time without any base being liberated.

Isomeric d-Hydrindamides of Phenyl-p-tolylphosphoric Acid.

The acid chloride was next treated with *d*-hydrindamine, as described in the case of the *dl*-base. The product, after preliminary purification, was fractionally crystallised from aqueous methyl alcohol, and after several operations the most sparingly soluble deposit underwent no further change in properties.

α -Isomeride.—The more sparingly soluble compound, distinguished as the α -isomeride, melted at 127°, and was analysed:

0·1652 gave 0·4216 CO₂ and 0·0888 H₂O. C = 69·6; H = 5·9.

C₂₂H₂₂O₃NP requires C = 69·65; H = 5·8 per cent.

0.3744, made up to 20 c.c., gave, in a 2-dcm. tube, $\alpha - 0.65^\circ$, whence $[\alpha]_D - 17.4^\circ$.

β -Isomeride.—The more readily soluble fractions, which separated from aqueous methyl alcohol in an oily condition, were dried and systematically crystallised from light petroleum (b. p. $65-75^\circ$); the most readily soluble portion was then again treated with aqueous methyl alcohol, and, after two crystallisations, the most sparingly soluble deposit was collected. This sample melted at $82-86^\circ$, and on analysis gave the following result:

0.1510 gave 0.3838 CO_2 and 0.0818 H_2O . C = 69.3; H = 6.0.

0.423, made up to 20 c.c., gave, in a 2-dcm. tube, $\alpha - 0.90^\circ$, whence $[\alpha]_D - 21.2^\circ$.

Although the specimen of the β -isomeride was certainly not a perfectly pure compound, these results prove beyond doubt that two isomeric amides are formed by the interaction of *d*-hydrindamine and phenyl-*p*-tolylphosphoryl chloride. The whole behaviour of the original product is that of a mixture of equal quantities of nearly related isomerides, and the isolation of the more readily soluble one was, of course, hardly to be expected; it was proved, however, that the β -isomeride was quite free from any hydrindamine salt, and in these circumstances the fact that it has a higher specific rotation than the α -isomeride is important proof of its real existence. Except for the difference in melting point and the slight difference in solubility, the two isomerides are very similar to one another and to the isomerides obtained with *dl*-hydrindamine; they both crystallise in prisms, and dissolve freely in alcohol and most other organic solvents, but are only sparingly soluble in cold light petroleum and practically insoluble in water. Their chemical behaviour is, of course, the same as that of the inactive isomerides, and both may be boiled with sodium carbonate in aqueous-alcoholic solution for some moments without any evolution of base taking place.

Attempts to reconvert the amides into the acids were not successful.

Isomeric l-Menthylamides of Phenyl-p-tolylphosphoric Acid.

These compounds were prepared and purified in a manner similar to that employed in the case of the hydrindamides. The crude, oily product which slowly solidified was fractionally crystallised from aqueous methyl alcohol, and after about three crystallisations the most sparingly soluble fraction began to crystallise in well-defined, prismatic needles.

α-Isomeride.—After about three more crystallisations, the most sparingly soluble fraction was a pure compound. On analysis:

0·1596 gave 0·4014 CO₂ and 0·1156 H₂O. C=68·6; H=8·06.

C₂₃H₃₂O₃NP requires C=68·8; H=7·98 per cent.

0·26, made up to 20 c.c., gave, in a 2-dcm. tube, α -0·84°, whence $[\alpha]_D$ -32·3°.

This *l*-menthylamide melts at 109—110°; it is soluble in alcohol, ethyl acetate, or chloroform, but is less readily soluble in ether or light petroleum.

β-Isomeride.—After removing the most sparingly soluble portions of the *l*-menthylamide, the remaining fractions all melted at temperatures ranging from 70—80°; as further fractional crystallisation from aqueous methyl alcohol proved to be useless, all these fractions were collected, dried, and dissolved in light petroleum. From this solvent, crystals could only be obtained with difficulty, owing to the great solubility of the substance, so after separating some more sparingly soluble material aqueous ethyl alcohol was employed; after protracted purification a sample, melting at 85—86°, was then obtained. This specimen gave the following result on analysis:

0·1548 gave 0·3916 CO₂ and 0·1134 H₂O. C=69·0; H=8·14.

C₂₃H₃₂O₃NP requires C=68·8; H=7·98 per cent.

0·2214, made up to 20 c.c., gave, in a 2-dcm. tube, α -0·84°, whence $[\alpha]_D$ -37·9°.

As in the case of the hydrindamides, this *β*-isomeride cannot be regarded as a perfectly pure substance. Nevertheless, the observations made during the examination of the menthylamides can only be explained on the assumption that the original product is a mixture of isomerides, apparently in equal quantities. The absence of any *l*-menthylamine salt from the *β*-isomeride was, of course, proved before analysis.

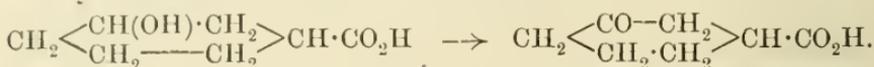
The isomeric *l*-menthylamides are very similar in properties, and are readily soluble in all common organic solvents, but are practically insoluble in water.

UNIVERSITY COLLEGE,
NOTTINGHAM.

CCXX.—*Synthesis of cycloHexanone-3-carboxylic Acid.*

By MARY ELIZABETH DOBSON, JOHN FERNS, and
WILLIAM HENRY PERKIN, jun.

THE synthesis of carvestrene (Perkin and Tattersall, *Trans.*, 1907, **91**, 480) had for its starting point *m*-hydroxybenzoic acid, which was reduced by sodium and alcohol to *cyclohexanol-3-carboxylic acid*, and the latter then converted into *cyclohexanone-3-carboxylic acid* by oxidation with chromic acid mixture:

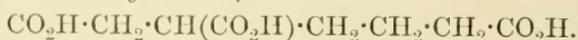


The yield of this ketonic acid was very unsatisfactory, and the preparation of the amount required for the synthesis of carvestrene proved to be so laborious that it was found impossible to investigate that important terpene and its derivatives in so thorough a manner as we had hoped to have done. In order, if possible, to overcome this difficulty, new experiments are being actively carried on, and the present communication deals with a series of reactions which have been undertaken with the object of synthesising *cyclohexanone-3-carboxylic acid*, and, although we have been successful in this, the process is, unfortunately, still not suitable for the preparation of large quantities of this acid. The various steps in the synthesis are the following.

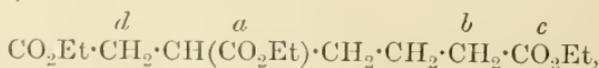
In the first place, ethyl oxaladipate is prepared by condensing ethyl oxalate with ethyl adipate in the presence of sodium ethoxide (compare Wislicenus and Schwanhäuser, *Annalen*, 1897, **297**, 110), and, on distilling this, it decomposes with elimination of carbon monoxide and formation of ethyl butane- $\alpha\delta\delta$ -tricarboxylate:



The sodium derivative of the latter ester reacts readily with ethyl bromoacetate, with the formation of *ethyl pentane- $\alpha\delta\delta\epsilon$ -tetracarboxylate*, $\text{CO}_2\text{Et·CH}_2\text{·C(CO}_2\text{Et)}_2\text{·CH}_2\text{·CH}_2\text{·CH}_2\text{·CO}_2\text{Et}$, and, when the product of the hydrolysis of this ester is heated, it yields *pentane- $\alpha\delta\epsilon$ -tricarboxylic acid*,

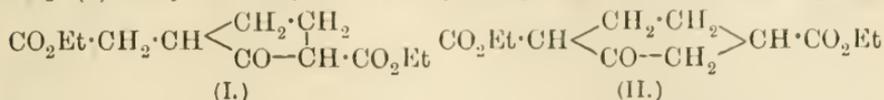


The next step was to investigate the action of sodium on the ester of this acid. When the formula of *ethyl pentane- $\alpha\delta\epsilon$ -tricarboxylate*,

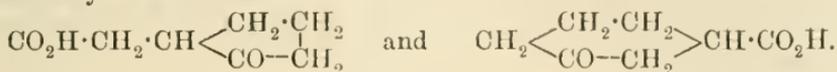


is examined, it is readily seen that condensation with elimination

of alcohol can take place either between the CO_2Et (*a*) and the CH_2 (*b*) to yield ethyl 5-carboxycyclopentanone-2-acetate (I), or

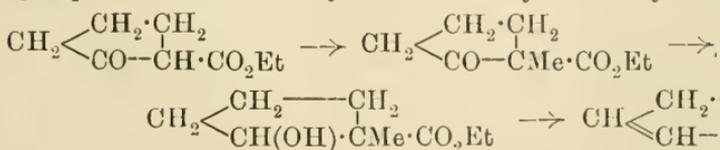


between the CO_2Et (*c*) and the CH_2 (*d*), in which case ethyl cyclohexanone-3:6-dicarboxylate (II) would be produced. On hydrolysis and elimination of carbon dioxide, the former would yield cyclopentanone-2-acetic acid, and the latter cyclohexanone-3-carboxylic acid:



Now, in condensations of this nature, where the two possibilities exist, the usual experience is that the five-carbon ring is almost invariably formed in preference to the six-carbon ring, and we were therefore greatly surprised when we found that the product of the action of sodium on ethyl pentane- $\alpha\delta\epsilon$ -tricarboxylate is evidently *ethyl cyclohexanone-3:6-dicarboxylate*. This is proved by the fact that the ester actually obtained yielded, on hydrolysis and elimination of carbon dioxide, an acid melting at 73—75°, which was proved, by direct comparison with a specimen of the acid prepared from *m*-hydroxybenzoic acid by Perkin and Tattersall (*loc. cit.*), to be *cyclohexanone-3-carboxylic acid*. These experiments therefore constitute a synthesis of this important acid, but the process is very costly and the yield too small to make the synthesis, in the meantime, of practical importance.

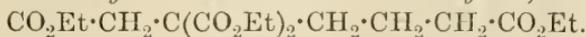
This communication also contains an account of an attempt to convert ethyl cyclopentanone-2-carboxylate into ethyl 1-methylcyclopentan-2-one-1-carboxylate, and then into ethyl 1-methylcyclopentan-2-ol-1-carboxylate and ethyl 1-methyl- Δ^2 -cyclopentene-



1-carboxylate, in order that the latter ester might be used in the further synthesis of terpenes containing a five-carbon ring (compare Haworth and Perkin, *Trans.*, 1908, **93**, 573).

EXPERIMENTAL.

Ethyl Pentane- $\alpha\delta\delta\epsilon$ -tetracarboxylate,



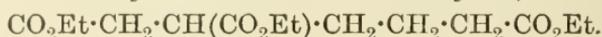
As explained on p. 2010, this ester is obtained when ethyl bromoacetate reacts with the sodium derivative of ethyl butane-

$\alpha\delta\delta$ -tricarboxylate, $\text{CH}(\text{CO}_2\text{Et})_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, an ester which we prepared in quantity by the method described by Wislicenus and Schwanhäuser (*loc. cit.*). Sodium (2.3 grams) was dissolved in absolute alcohol (40 grams), mixed with ethyl butane- $\alpha\delta\delta$ -tricarboxylate (27.4 grams) and ethyl bromoacetate (16.7 grams), and the whole heated in a reflux apparatus on the water-bath for two hours. The product was mixed with water, extracted with ether, the ethereal solution washed, dried, and evaporated, and the residual oil several times fractionated under diminished pressure, when a considerable quantity of a colourless oil distilled at $210\text{--}212^\circ/10$ mm., and consisted of pure *ethyl pentane- $\alpha\delta\delta\epsilon$ -tetracarboxylate*:

0.2112 gave 0.4371 CO_2 and 0.1519 H_2O . C=56.4; H=8.0.

$\text{C}_{17}\text{H}_{28}\text{O}_8$ requires C=56.7; H=7.8 per cent.

Ethyl Pentane- $\alpha\delta\epsilon$ -tricarboxylate,



In order, in the first place, to obtain pentane- $\alpha\delta\epsilon$ -tricarboxylic acid, ethyl pentane- $\alpha\delta\delta\epsilon$ -tetracarboxylate was boiled with a mixture of three times its volume of concentrated hydrochloric acid, diluted with an equal volume of water, for seventeen hours in a reflux apparatus, the condenser of which was removed from time to time to allow alcohol to escape. The hydrochloric acid was then distilled off under diminished pressure, and the syrupy residue heated in an oil-bath until the evolution of carbon dioxide ceased. The crude pentane- $\alpha\delta\epsilon$ -tricarboxylic acid thus obtained was esterified by digesting with alcohol and sulphuric acid for several hours, the ester was then precipitated with water, extracted with ether, the ethereal solution washed with sodium carbonate, dried, and fractionated, when almost the whole quantity distilled at $195\text{--}197^\circ/15$ mm., and consisted of pure *ethyl pentane- $\alpha\delta\epsilon$ -tricarboxylate*:

0.1502 gave 0.3212 CO_2 and 0.1134 H_2O . C=58.3; H=8.4.

$\text{C}_{14}\text{H}_{24}\text{O}_6$ requires C=58.3; H=8.3 per cent.

When this ester was digested with dilute hydrochloric acid, it was readily hydrolysed, and, after distilling off the hydrochloric acid under diminished pressure, a syrup remained which gradually crystallised.

The mass was left in contact with porous porcelain until quite dry, and then crystallised from a very little hydrochloric acid, in which the acid is very readily soluble. The following analyses were made with different preparations; the first was carried out with a specimen of the acid which had remained for some days simply exposed to the air, and the second with a specimen of the

acid which had been dried for twenty-four hours over sulphuric acid:

0.1135 gave 0.1890 CO₂ and 0.0640 H₂O. C = 45.4; H = 6.3.

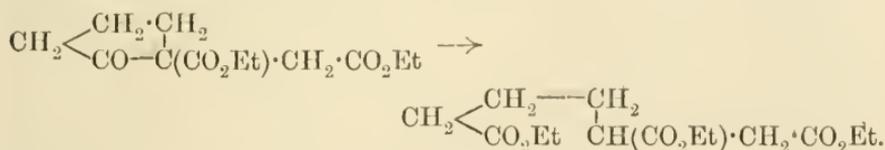
0.1260 ,, 0.2100 CO₂ ,, 0.0710 H₂O. C = 45.4; H = 6.3.

C₈H₁₂O₆, $\frac{1}{2}$ H₂O requires C = 45.1; H = 6.1 per cent.

It appears, therefore, from these analyses, that *pentane- $\alpha\delta\epsilon$ -tricarboxylic acid* crystallises from hydrochloric acid with $\frac{1}{2}$ H₂O.

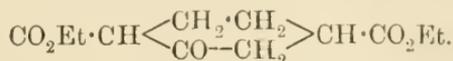
It crystallises in crusts, melts at about 96°, and, on cooling, sets to a resin which remains in that condition for months.

Ethyl pentane- $\alpha\delta\epsilon$ -tricarboxylate has been obtained by Kötze and Schüler (*Annalen*, 1906, **350**, 241) by treating the sodium derivative of ethyl *cyclopentanone-2-carboxylate* with ethyl bromoacetate and then hydrolysing the ethyl *cyclopentanone-2-carboxylate-2-acetate* thus produced with sodium ethoxide, when fission of the ring takes place according to the scheme:



These investigators give the boiling point of ethyl pentane- $\alpha\delta\epsilon$ -tricarboxylate as 188—189°/18 mm., which is rather lower than the boiling point (195—197°/15 mm.) recorded by us. They also hydrolysed the ester with hydrochloric acid, but were unable to obtain the acid in a crystalline condition; they, however, describe a crystalline anhydride, C₈H₁₀O₅, which melted at 95°.

Ethyl cyclohexanone-3: 6-dicarboxylate,



This ester is produced when sodium reacts with ethyl pentane- $\alpha\delta\epsilon$ -tricarboxylate under the following conditions.

In a flask fitted with a ground-in condenser tube, sodium (4.7 grams) is melted under boiling toluene, vigorously shaken, and, when cold, the toluene is decanted from the "molecular sodium," the latter washed with benzene, mixed with 150 c.c. of dry benzene, and then ethyl pentane $\alpha\delta\epsilon$ -tricarboxylate (30 grams) added, and the whole heated on the water-bath for three hours. The brown product is mixed with ether (400 c.c.) and excess of dilute hydrochloric acid, the ether-benzene solution well washed, dried, and the ether and benzene distilled off. The brown oil which remained was twice fractionated, when a good yield of a colourless oil was

obtained which distilled at 175—180°/20 mm., but apparently with slight decomposition, since the analytical results agreed only approximately with the theoretical:

0·1655 gave 0·3524 CO₂ and 0·1201 H₂O. C=58·1; H=8·1.

0·1096 „ 0·2335 CO₂ „ 0·0782 H₂O. C=58·1; H=7·9.

C₁₂H₁₈O₃ requires C=59·5; H=7·5 per cent.

Ethyl cyclohexanone-3:6-dicarboxylate has an odour somewhat resembling that of ethyl acetoacetate, and gives in alcoholic solution a purple coloration on the addition of ferric chloride.

Synthesis of cycloHexanone-3-carboxylic Acid,



As explained on p. 2011, this acid is produced when ethyl *cyclohexanone-3:6-dicarboxylate* is hydrolysed with hydrochloric acid.

The crude ester is boiled in a reflux apparatus with a considerable quantity of 2 per cent. hydrochloric acid for about three days, and until a small quantity, after extraction with ether, gives no coloration with ferric chloride. The clear solution is saturated with ammonium sulphate, extracted many times with ether, the ethereal solution dried, evaporated, and the crude dark brown ketonic acid (20 grams) converted into the ester by leaving it in contact with alcoholic hydrogen chloride (75 c.c. of a 2 per cent. solution) at the ordinary temperature. After three or four days, the bulk of the alcohol is removed by distillation under diminished pressure, the residue mixed with water, extracted with ether, the ethereal solution well washed, dried, and evaporated, and the ester purified by distillation, when almost the whole quantity passes over at 135—137°/20 mm. (compare Perkin and Tattersall, *Trans.*, 1907, 91, 491):

0·1086 gave 0·2565 CO₂ and 0·0842 H₂O. C=64·1; H=8·6.

0·1019 „ 0·2372 CO₂ „ 0·0795 H₂O. C=63·0; H=8·5.

C₉H₁₄O₃ requires C=63·5; H=8·2 per cent.

This ethyl *cyclohexanone-3-carboxylate* was digested with 50 c.c. of a 2·5 per cent. solution of hydrochloric acid until a clear solution resulted, ammonium sulphate was then added, and the whole very thoroughly extracted with ether. The ethereal extract, after drying and evaporating, yielded a viscid syrup, which distilled at 195—197°/20 mm., and the distillate gradually crystallised.

In contact with porous porcelain, traces of oily impurity were rapidly removed, and the residue separated from benzene in small, glistening prisms, which melted at 73—75°, whereas the melting

point of *cyclohexanone-3-carboxylic acid* is stated by Perkin and Tattersall (*loc. cit.*, p. 492) to be 75—76°:

0.1392 gave 0.3001 CO₂ and 0.0864 H₂O. C=58.8; H=6.9.

C₇H₁₀O₃ requires C=59.1; H=7.0 per cent.

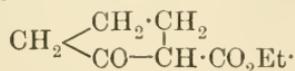
The semicarbazone.—When an aqueous solution of the acid was mixed with semicarbazide hydrochloride and sodium acetate there was no immediate precipitation of the semicarbazone, but, on long standing, this derivative separated as a sandy powder, which, after crystallisation from methyl alcohol, melted and decomposed at 183—184°:

0.0699 gave 12.7 c.c. N₂ at 14° and 767 mm. N=21.6.

C₅H₁₃O₃N₃ requires N=21.2 per cent.

The properties of the ketonic acid are therefore exactly those of *cyclohexanone-3-carboxylic acid* described by Perkin and Tattersall (*loc. cit.*), and the identity of the specimens, prepared in such different ways, was confirmed by the fact that, when intimately mixed, there was no alteration in melting point.

Ethyl cyclopentanone-2-carboxylate,



This ester was first prepared by Dieckmann (*Ber.*, 1894, **27**, 103) by the action of sodium on ethyl adipate and a little alcohol at 120°, but, as the result of several experiments, we have found that the reaction is best carried out under the following conditions.

Sodium (11.5 grams) is melted under boiling toluene and vigorously shaken, the whole is then allowed to cool, the toluene decanted from the "molecular" sodium, and then a solution of ethyl adipate (50 grams) in dry benzene (100 c.c.) is added, and the whole heated on the water-bath in a reflux apparatus for two hours. The product is mixed with ether, decomposed with ice and dilute hydrochloric acid, the ether-benzene solution washed, dried, and evaporated, and the residual oil fractionated under diminished pressure, when almost the whole quantity distils constantly at 132°/30 mm. The distillate, which was obtained in a yield of 27 grams, gave a blue coloration when ferric chloride was added to its alcoholic solution:

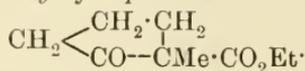
0.1302 gave 0.2924 CO₂ and 0.0913 H₂O. C=61.3; H=7.8.

C₈H₁₂O₃ requires C=61.5; H=7.7 per cent.

Wislicenus and Schwanhäuser (*Annalen*, 1897, **297**, 112) state that ethyl *cyclopentanone-2-carboxylate* distils at 120°/22 mm. When this ester (25 grams) was added to a solution of magnesium methyl iodide (containing 7.7 grams of magnesium) a vigorous

action took place, and the yellow magnesium derivative, which first separated, soon became colourless. The product, isolated in the usual manner, and hydrolysed with alcoholic potassium hydroxide, yielded adipic acid, and there was no evidence that any hydroxymethyl acid had been produced. It is obvious, therefore, that ethyl *cyclopentanone-2-carboxylate* reacts with magnesium methyl iodide as an enolic modification.

Ethyl 1-Methylcyclopentan-2-one-1-carboxylate,



This ester has already been described by Bouveault (*Bull. Soc. chim.*, 1899, [iii], **21**, 1019), who obtained it from the sodium derivative of ethyl *cyclopentanone-2-carboxylate* by the action of methyl iodide, and he states that it distils at $108^\circ/22$ mm. We have prepared it in considerable quantities by the same process, and observed the somewhat higher boiling point, $120\text{--}122^\circ/30$ mm.:

0.126 g gave 0.2932 CO_2 and 0.0918 H_2O . C=63.5; H=8.1.

$\text{C}_9\text{H}_{14}\text{O}_3$ requires C=63.5; H=8.2 per cent.

Ethyl 1-methyl*cyclopentan-2-one-1-carboxylate* is a colourless oil with a pleasant odour; it gives no coloration with ferric chloride.

Reduction with Sodium Amalgam.—The results obtained in our experiments on the reduction of the above ketonic ester with sodium amalgam varied very much; in some cases the reduction appeared to proceed normally, with the formation of 1-methyl*cyclopentan-2-ol-1-carboxylic acid*, whilst, in other cases, the ketonic ester suffered hydrolysis with formation of methyladipic acid. On one occasion, an experiment, carried out under the following conditions, appeared to proceed normally. The pure ketonic ester (20 grams), dissolved in dilute alcohol, was treated in the cold with 1 kilo. of freshly prepared sodium amalgam (3 per cent.), hydrochloric acid being added from time to time in such a way that the solution was always nearly neutral. The product was acidified, saturated with ammonium sulphate, extracted twelve times on the machine, the extracts were combined, dried, evaporated, and the residue esterified by warming on the water-bath with alcoholic sulphuric acid (10 per cent.) for six hours. The ester, isolated in the usual manner, distilled at $158\text{--}160^\circ/100$ mm., and gave the following results, which agree fairly well with those required for ethyl 1-methyl*cyclopentan-2-ol-1-carboxylate*:

0.1721 gave 0.3926 CO_2 and 0.1411 H_2O . C=62.3; H=9.1.

$\text{C}_9\text{H}_{16}\text{O}_3$ requires C=62.8; H=9.3 per cent.

When this ester was boiled for three hours with three times

its volume of acetic anhydride, an oil was obtained which distilled at 147—151°/40 mm., and yielded numbers agreeing closely with those required for ethyl 2-acetoxy-1-methylcyclopentane-1-carboxylate:

0.1731 gave 0.3907 CO₂ and 0.1318 H₂O. C=61.5; H=8.5.

C₁₁H₁₈O₄ requires C=61.7; H=8.4 per cent.

Some of the ethyl 1-methylcyclopentan-2-ol-1-carboxylate was heated with two molecular proportions of phosphorus pentachloride for one and a-half hours on the sand-bath, and the product poured into alcohol. The ester thus obtained distilled at 160—170°/40 mm., and, on analysis:

0.1696 gave 0.1504 AgCl. Cl=21.9,

whereas ethyl 2-chloro-1-methylcyclopentane-1-carboxylate contains 18.3 per cent. of chlorine. This chloro-ester proved to be remarkably stable, since it was scarcely attacked by boiling with diethylaniline, and, as all our other attempts to eliminate hydrogen chloride and to obtain the corresponding unsaturated ester were unavailing, the subject was not further investigated.

THE UNIVERSITY,
MANCHESTER.

CCXXI.—*The Acyl-bornylamines. Part I. Fatty Bornylamides.*

By PERCY FARADAY FRANKLAND and FRED BARROW.

In order to determine the effect of substitution on the rotatory power of optically active compounds, attention has already been directed by one of us to an examination of active amides and their substitution products (Frankland, Wharton, and Aston, *Trans.*, 1901, **79**, 266; Frankland and Slator, *ibid.*, 1903, **83**, 1349; Frankland and Ormerod, *ibid.*, 1903, **83**, 1342; Frankland and Done, *ibid.*, 1906, **89**, 1859; and Frankland and Twiss, *ibid.*, 1906, **89**, 1852). All these investigations have had as their starting point the amide of an active acid (glyceric, malic, or tartaric), and the effect of substitution of the hydrogen of the amido-group by various radicles on the rotatory power has been examined.

Amides derived from optically active amines have, however, received comparatively little attention. Numerous acyl derivatives—chiefly acetyl and benzoyl—have, indeed, been described, but very little systematic work has been* done on the substitution of the

hydrogen of the amino-group of active amines by negative groups. The only amines which have been studied from this point of view are *d*- and *l*-menthylamines and *l*-fenchylamine. Of these, the formyl, acetyl, propionyl, and butyryl derivatives were prepared by Binz, and their rotations in solution examined (*Zeitsch. physikal. Chem.*, 1893, **12**, 723).

With the object of studying the effect of substitution on the rotatory power of an active amine, we have examined the optical properties of some derivatives of bornylamine, formed by replacing the amino-hydrogen by various aliphatic and aromatic acyl groups.

Bornylamine was first obtained by Leuckhart and Bach (*Ber.*, 1887, **20**, 104) by heating camphor with ammonium formate, and subsequent hydrolysis of the resulting formobornylamide. The formyl, acetyl, and benzoyl derivatives were described, but no account of their optical behaviour was given.

Forster (*Trans.*, 1898, **73**, 386) obtained bornylamine by the reduction of camphoroxime with sodium in amyl-alcoholic solution. He showed that the base, obtained either by heating camphor with ammonium formate, or by reduction of the oxime, was not a single chemical individual, but consisted of a mixture of two stereoisomeric amines having rotations of opposite sign, which can be readily separated by taking advantage of the difference in the solubility of their hydrochlorides.

Dextrorotatory bornylamine, the hydrochloride of which is the less soluble, is the more easily obtained, and Forster (*Trans.*, 1899, **75**, 934, 1149) prepared a large number of its derivatives, more particularly investigating the alkyl-bornylamines as well as the condensation products which it forms with aromatic aldehydes. The acyl-bornylamines examined by him are given below, together with their rotations in ethyl-alcoholic solution.

Rotation in Ethyl-Alcoholic Solution (Forster).

	<i>c.</i>	<i>t.</i>	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
Formobornylamide	3.5672	20°	-42.1°	-76.2°
Acetobornylamide	2.9260	20	42.9	83.6
Benzobornylamide	4.0052	20	21.8	55.9
Benzomethylbornylamide.	1.7716	24	65.5	177.5
Benzooethylbornylamide ...	2.7612	21	65.2	185.7
Benzopropylbornylamide	1.9608	14	60.4	180.5

The present communication deals with the preparation and properties of the formo-, aceto-, propiono-, and *n*-butyro-bornylamides.

The formo- and aceto-compounds, which have previously been described by Forster, were prepared by heating bornylamine with the corresponding acid, whilst the propiono- and butyro-derivatives

were obtained by the interaction of bornylamine and the acid chloride in ethereal solution.

The rotatory powers were, in all cases, determined in methyl and ethyl alcohol, as well as in pyridine and glacial acetic acid solution. The observations were all made at 20°, and on solutions of approximately 5 and 10 per cent. strength.

The results of the polarimetric determinations are summarised in the following table:

<i>p</i> (approx.)	Formo- bornylamide.		Aceto- bornylamide.		Propiono- bornylamide.		<i>n</i> -Butyro- bornylamide.	
	$[\alpha]_D^{20}$.	$[M]_D^{20}$.	$[\alpha]_D^{20}$.	$[M]_D^{20}$.	$[\alpha]_D^{20}$.	$[M]_D^{20}$.	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
<i>Ethyl-Alcoholic Solution.</i>								
5	-43·17°	-78·14°	-43·48°	-84·79°	-40·79°	-85·25°	-37·73°	-84·14°
<i>Methyl-Alcoholic Solution.</i>								
5	-40·88°	-73·99°	-41·93°	-81·76°	-38·68°	-80·84°	-35·73°	-79·65°
10	41·01	74·23	42·10	82·10	39·48	82·51	35·86	79·97
<i>Glacial Acetic Acid Solution.</i>								
5	-13·80°	-24·99°	-34·80°	-67·85°	-37·19°	-77·72°	-34·89°	-77·80°
10	15·30	27·69	36·14	70·47	37·54	78·46	35·29	78·70
<i>Pyridine Solution.</i>								
5	-16·96°	-30·70°	-11·97°	-23·32°	-14·64°	-30·60°	-12·57°	-28·03°
10	18·60	33·67	15·14	29·52	16·38	34·23	15·06	33·58

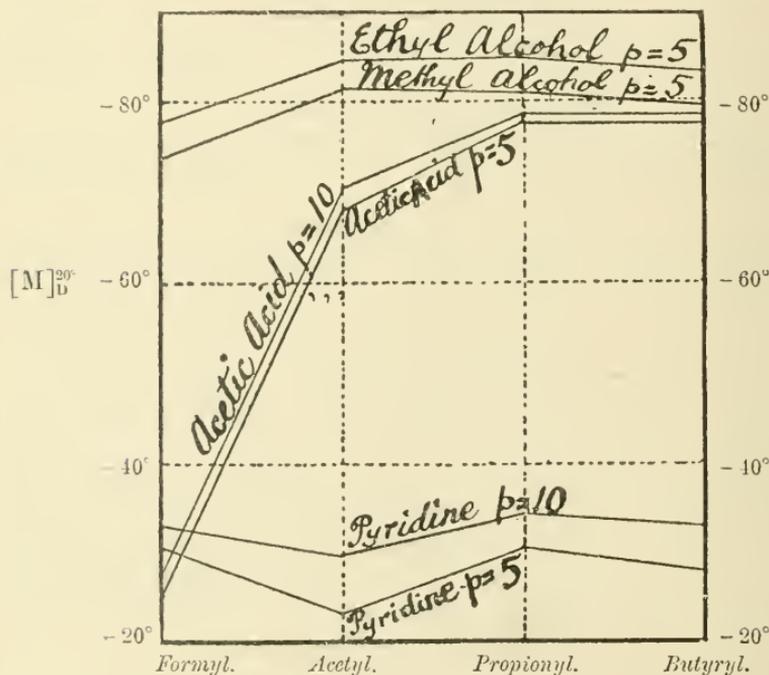
The relationship existing between the molecular rotations of the various members of the series is more readily seen from the accompanying diagram. It will be observed that the rotatory powers of the aliphatic acyl-bornylamides, which we have investigated, depend to a very great extent on the nature of the solvent in which they are examined. These substances show the greatest rotatory power in ethyl-alcoholic solution, and, with the exception of the formo-derivative, the smallest in pyridine. The alteration, however, in the rotatory power of these acyl-bornylamines, caused by the change in the nature of the solvent, varies considerably with each member of the series. In methyl alcohol, ethyl alcohol, and glacial acetic acid solution, the activity of the formo-derivative shows by far the greatest variation, the value of the molecular rotation falling from -78·14° in ethyl-alcoholic solution to -24·99° in glacial acetic acid—a difference of 53·15°; in the case of the butyro-compound, on the other hand, the alteration in the rotatory power in the same solvents is smaller than that observed with the other members of the series, the molecular rotation falling from -84·14° in ethyl

alcohol to -77.80° in glacial acetic acid solution—a difference of only 6.34° .

Thus the variation in the rotatory power brought about by change in the nature of the solvent becomes less and less marked as the series is ascended. This gradual diminution in the effect of the solvent is very clearly shown in the diagram by the convergence of the curves marked ethyl alcohol, methyl alcohol, and acetic acid, as we pass from the lowest to the higher members of the series.

It may also be pointed out that all these aliphatic acyl-bornylamines have a greater rotation in ethyl alcohol than in methyl

Molecular rotation of the aliphatic bornylamines in pyridine, ethyl and methyl alcohol, and acetic acid solution.



alcohol, and again a greater rotation in methyl alcohol than in glacial acetic acid solution, whilst the rotation in pyridine is, excepting in the case of formobornylamide, less than in any of the other solvents. The rotatory power of these substances in the different solvents is also influenced by the concentration, but the variation thus produced is very small, excepting in the case of pyridine. In all cases, however, increase in concentration is attended by increased rotatory power.

It is particularly noteworthy that in this series of the aliphatic acyl-bornylamines the maximum molecular rotation does not

uniformly fall on the same term of the series, but its position varies according to the solvent employed. Thus in both methyl- and ethyl-alcoholic solutions the maximum occurs on the second term; in glacial acetic acid solution, on the other hand, the rapid increase in the rotatory power shown between formo- and aceto-bornylamide is maintained up to the propiono-derivative, which does not materially differ in rotatory power from the butyro-compound, and thus represents the maximum.

Turning now to the rotatory powers in pyridine solution, it will be observed that these show much less regularity than those in the other solvents. Instead of rising continuously to a maximum and then gradually diminishing or remaining constant, as in the case of the alcoholic and glacial acetic acid solutions, the molecular rotations in pyridine solution show an alternation of high and low values. This irregular behaviour of the aliphatic acyl-bornylamines in pyridine is undoubtedly to be referred to an irregularity in the influence of the solvent on the first member of the series. It has already been pointed out that the aceto-, propiono-, and *n*-butyro-bornylamides have a greater rotatory power in methyl-alcoholic than in glacial acetic acid solution, and, again, a greater rotatory power in acetic acid than in pyridine. Moreover, the same regularity has been observed in the rotatory powers of the seven aromatic acyl-bornylamines described in the following communication. With the formyl derivative, however, this is no longer the case, the molecular rotation in pyridine solution being greater than that in glacial acetic acid solution. Owing to some disturbing influence of the solvent, the rotatory power of the first member in pyridine solution is thus much higher than was to be anticipated from a consideration of the behaviour of the other members. It may, however, be pointed out that if the first term of the series be neglected, then the molecular rotatory powers of the succeeding aliphatic acyl-bornylamines in pyridine solution show the same behaviour as in the other solvents, in that they attain a limiting value at the acetyl or propionyl term.

As regards the influence of substitution on the rotatory power of bornylamine, it is observed that the acyl group exerts a marked lævorotatory effect. The dependence of the rotatory power on the qualitative nature of the substituting group is shown in the following table, in which the rotatory powers of the corresponding alkyl- and acyl-bornylamines in ethyl-alcoholic solution are contrasted:

*Rotations in Ethyl-Alcoholic Solution.**Bornylamine*: $p = 5.006$, $[M]_D^{20} + 72.51^\circ$.

Acyl-				Alkyl-			
bornylamines.	p .	t° .	$[M]_D$.	bornylamines.†	c .	t° .	$[M]_D$.
Formo-	4.9984	20°	-78.14°	Methyl	2.0256	23°	+135.3°
Aceto-	4.9380	20	84.79	Ethyl	2.6728	15	136.4
Propiono- ...	5.0013	20	85.25	<i>n</i> -Propyl	2.0840	16	140.4
—	—	—	—	<i>iso</i> Propyl	2.0140	16	123.4
<i>n</i> -Butyro- ...	5.0021	20	84.14	<i>n</i> -Butyl	1.9932	16	135.4
Benzo-*	4.9940	20	58.93	Benzyl	2.2284	20	184.0
<i>o</i> -Nitrobenzo-*	4.9799	20	67.62	<i>o</i> -Nitrobenzyl	2.0272	22	176.2
<i>m</i> -Nitrobenzo-*	2.6399	20	84.29	—	—	—	—
<i>p</i> -Nitrobenzo-*	4.2770	20	50.58	<i>p</i> -Nitrobenzyl	2.0148	22	191.8
<i>o</i> -Toluo-* ...	5.0002	20	51.60	—	—	—	—
<i>m</i> -Toluo-* ...	5.0073	20	60.70	—	—	—	—
<i>p</i> -Toluo-*	5.0187	20	39.43	—	—	—	—

* See following communication.

† Forster, *Trans.*, 1899, **75**, 934.

Introduction of a positive radicle increases the dextrorotation of bornylamine, whereas the corresponding acyl group exerts such a marked levorotatory effect that its introduction is in all cases attended by a complete change in the sign of the rotation.

EXPERIMENTAL.

The bornylamine used in these experiments was prepared by reducing camphoroxime with sodium in amyl-alcoholic solution; the hydrochlorides of the mixed amines so produced were recrystallised from water until of constant rotatory power.

The following polarimetric values were obtained for the hydrochloride and free amine in two different preparations:

Rotatory Power of Bornylamine Hydrochloride.

p .	d 20°/4°.	l in mm.	α_D^{20} .	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
-------	-------------	------------	-------------------	---------------------	----------------

Ethyl-Alcoholic Solution.

Prep. I	4.868	0.8032	299.3	+2.66°	+22.73°	+42.85°
„ II	5.213	0.8034	299.3	2.84	22.66	42.73

*Rotatory Power of Bornylamine.**Ethyl-Alcoholic Solution.*

Prep. I	5.0557	0.7949	299.3	+5.68°	+47.22°	+72.22°
„ II	5.0060	0.7972	299.3	5.66	47.39	72.51

The value given above for the rotatory power of the amine is rather higher than that found by Forster, namely, $[\alpha]_D^{20} + 45.5^\circ$, $c = 4.0496$.

Formobornylamide.

This compound was prepared in the manner given by Forster, by heating bornylamine with several times its weight of anhydrous formic acid for some hours, and purified by crystallising from dilute alcohol until it possessed a constant rotatory power.

It forms lustrous, flat plates, which possess no definite melting point, but begin to soften at 83°, and are not completely melted until 91°. It is readily soluble in alcohol, pyridine, glacial acetic acid, or benzene:

0.1592 gave 10.7 c.c. N₂ (moist) at 13.5° and 750 mm. N = 7.80.

C₁₁H₁₉ON requires N = 7.73 per cent.

Rotatory Power of Formobornylamide.

p. *d* 20°/4°. *l* in mm. $\alpha_D^{20^\circ}$. $[\alpha]_D^{20^\circ}$. $[M]_D^{20^\circ}$.

Ethyl-Alcoholic Solution.

5.3155	0.8003	199.84	-3.67°	-43.17°	-78.14°
4.9984	0.8001	199.84	3.45	43.17	78.14

Methyl-Alcoholic Solution.

4.9747	0.8046	389.9	-6.38°	-40.88°	-73.99°
9.9845	0.8127	199.84	6.65	41.01	74.23

Glacial Acetic Acid Solution.

5.5607	1.0496	199.84	-1.61°	-13.80°	-24.99°
9.6903	1.0499	199.84	3.11	15.30	27.69

Pyridine Solution.

5.0156	0.9800	389.9	-3.25°	-16.96°	-30.70°
10.0200	0.9829	199.84	3.66	18.60	33.67

The value found by us for the rotation in ethyl-alcoholic solution is slightly greater than that found by Forster, namely, $[\alpha]_D^{20^\circ} - 42.1^\circ$, $c = 3.5672$.

The formobornylamide employed in the above polarimetric determinations melted indefinitely at 83—91°; Forster gives the melting point of this compound as 93°. It was therefore considered advisable to repeat the preparation, but we have only been able to confirm our earlier result. The details of the experiment are given below. Eight grams of bornylamine were dissolved in 50 grams of anhydrous formic acid, and the mixture heated to boiling for nine hours. The formobornylamide (7.5 grams) was precipitated by pouring into water and crystallised from dilute alcohol, melting point 82—92°. On crystallising a second time from the same solvent, the compound melted at 81—91°, and gave the following polarimetric values in methyl-alcoholic solution:

$p = 10.066$, d 20°/4° = 0.8191, $l = 199.84$ mm., $\alpha_D^{20^\circ} - 6.72^\circ$, $[\alpha]_D^{20^\circ} - 40.79^\circ$.

The product was again recrystallised from dilute alcohol. It again melted at 81—91°, and gave the following polarimetric results in methyl-alcoholic solution :

$p = 10\cdot001$, $d_{20^\circ/4^\circ} = 0\cdot8176$, $l = 199\cdot84$ mm., $\alpha_D^{20^\circ} = 6\cdot66^\circ$, $[\alpha]_D^{20^\circ} = 40\cdot76^\circ$.

The above rotatory powers are identical and agree very closely with those already given for the first preparation. Further crystallisation from alcohol or light petroleum produced no change in the melting point. The bornylamine used in these preparations had a specific rotation of $+47\cdot37^\circ$ in ethyl-alcoholic solution—a value rather higher than that given by Forster. The indefinite melting point observed by us for the formo-derivative cannot, therefore, be referred to admixture of formoneobornylamide, for the presence of the neo-base in the original amine would have diminished the dextro-rotation.

Acetobornylamide.

This was also prepared in the same manner as that described by Forster, namely, by boiling bornylamine with several times its weight of glacial acetic acid, to which a few drops of acetic anhydride had been added. The mixture was poured into water, and the acetobornylamide, separating out, recrystallised from a mixture of benzene and light petroleum. It is thus obtained in small, flat plates, melting at $145\cdot5^\circ$, readily soluble in alcohol, ethyl acetate, benzene, or acetone, but only sparingly so in light petroleum :

0.1997 gave 15.2 c.c. N_2 (moist) at 11° and 762.5 mm. $N = 7\cdot26$.

$C_{12}H_{21}ON$ requires $N = 7\cdot18$ per cent.

Rotatory Power of Acetobornylamide.

p .	$d_{20^\circ/4^\circ}$.	l in mm.	$\alpha_D^{20^\circ}$.	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.
<i>Ethyl-Alcoholic Solution.</i>					
4.938	0.7998	199.84	$-3\cdot43^\circ$	$-43\cdot48^\circ$	$-84\cdot79^\circ$
<i>Methyl-Alcoholic Solution.</i>					
5.005	0.8055	199.84	$-3\cdot38^\circ$	$-41\cdot93^\circ$	$-81\cdot76^\circ$
10.088	0.8150	199.84	6.92	42.10	82.10
<i>Glacial Acetic Acid Solution.</i>					
4.958	1.049	199.84	$-3\cdot63^\circ$	$-34\cdot93^\circ$	$-68\cdot11^\circ$
5.014	1.049	199.84	3.64	34.65	67.58
10.021	1.048	99.9	3.79	36.14	70.47
<i>Pyridine Solution.</i>					
4.904	0.9790	389.9	$-2\cdot24^\circ$	$-11\cdot97^\circ$	$-23\cdot32^\circ$
10.015	0.9800	199.84	2.97	15.14	29.52

The value obtained by us for the rotation of acetobornylamide in ethyl-alcoholic solution agrees very closely with that given by Forster, namely, $[\alpha]_D^{20} - 42.9^\circ$, $c = 2.9260$.

Propionobornylamide.

Twelve grams of bornylamine were dissolved in 100 c.c. of ether, and an ethereal solution of propionyl chloride slowly run in. A dilute solution of sodium hydroxide in water was then added, and the mixture well shaken in order to decompose the bornylamine hydrochloride, which separated out. Addition of propionyl chloride was then continued until about one and a-half times the calculated amount had been added. On evaporating the ethereal solution, a colourless oil was left behind, and this quickly solidified to a white, crystalline mass. The propionobornylamide was purified by dissolving in acetone, adding water until a permanent turbidity was almost produced, and then allowing the acetone partly to evaporate at the ordinary temperature. It is thus obtained in small, flat, colourless needles, which begin to soften at 110° and melt at 117° . It is readily soluble in benzene, light petroleum, chloroform, acetone, or alcohol, and separates from hot solvents in the form of an oil:

0.2104 gave 12.4 c.c. N_2 (moist) at 13° and 745.6 mm. $N = 6.82$.
 $C_{13}H_{23}ON$ requires $N = 6.70$ per cent.

Rotatory Power of Propionobornylamide.

<i>p.</i>	<i>d</i> $20^\circ/4^\circ$.	<i>l</i> in mm.	α_D^{20} .	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
<i>Ethyl-Alcoholic Solution.</i>					
5.0047	0.7983	389.9	-6.30°	-40.44°	-84.52°
5.0013 (recryst.)	0.7982	389.9	6.35	40.79	85.25
<i>Methyl-Alcoholic Solution.</i>					
5.0055	0.8028	389.9	-6.06°	-38.68°	-80.84°
9.9974	0.8113	199.84	6.40	39.48	82.51
<i>Glacial Acetic Acid Solution.</i>					
5.0249	1.047	389.9	-7.63°	-37.19°	-77.72°
10.0087	1.045	199.84	7.85	37.54	78.46
<i>Pyridine Solution.</i>					
4.9970	0.9780	389.9	-2.79°	-14.64°	-30.60°
9.9805	0.9797	199.84	3.20	16.38	34.23

n-Butyrobornylamide.

This was prepared by the interaction of *n*-butyryl chloride and bornylamine in ethereal solution in a similar manner to that

described for the propiono-compound. On evaporation of the ether, butyroborylamide was obtained as a viscid, colourless oil, which quickly solidified on cooling. It was finely powdered and shaken with dilute sodium carbonate for about three hours in order to remove butyric acid and chloride. On crystallisation from acetone, butyroborylamide was obtained in small plates, melting at 97°. It is readily soluble in alcohol, chloroform, ethyl acetate, or pyridine, and less so in benzene :

0.2587 gave 13.75 c.c. N₂ (moist) at 12° and 766.9 mm. N = 6.36.
C₁₄H₂₅ON requires N = 6.28 per cent.

Rotatory Power of n-Butyroborylamide.

<i>p.</i>	<i>d</i> 20°/4°.	<i>l</i> in mm.	$\alpha_D^{20^\circ}$.	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.
-----------	------------------	-----------------	-------------------------	---------------------------	----------------------

Ethyl-Alcoholic Solution.

4.7930	0.7980	199.84	-2.89°	-37.81°	-84.31°
5.0021	0.7980	199.84	3.01	37.73	84.14

Methyl-Alcoholic Solution.

4.9780	0.8047	199.84	-2.86°	-35.73°	-79.65°
10.009	0.8131	199.84	5.83	35.86	79.97

Glacial Acetic Acid Solution.

5.0337	1.048	199.84	-3.68°	-34.89°	-77.80°
10.016	1.044	199.84	7.38	35.29	78.70

Pyridine Solution.

4.921	0.9783	389.9	-2.36°	-12.57°	-28.03°
10.005	0.9796	199.84	2.95	15.06	33.58

UNIVERSITY,
BIRMINGHAM.

CCXXII.—*The Acyl-bornylamines. Part II. Aromatic Bornylamides.*

By PERCY FARADAY FRANKLAND and FRED BARROW.

IN the foregoing communication the optical activity of some derivatives of bornylamine formed by the substitution of the aminic hydrogen atom by aliphatic acyl groups has been described. In the present communication we have confined our attention to the aromatic acyl derivatives, having prepared and examined the rotations of the benzo-, the three toluo-, and the three nitrobenzo-bornylamides, firstly as a contribution to the study of the relation-

ship between position-isomerism and optical activity, and secondly with the object of comparing the rotatory effect of the methyl and nitro-groups when substituted in the ortho-, meta-, and para-positions of the benzene ring.

Of these derivatives, only benzobornylamide has been previously prepared (Forster, *Trans.*, 1898, **73**, 393). The aromatic bornylamides described in the present paper were all prepared by the interaction of ethereal solutions of the acid chloride and bornylamine in the presence of an aqueous solution of potassium hydroxide.

The rotatory powers were determined in the same solvents as those employed in the case of the aliphatic bornylamides, namely, ethyl alcohol, methyl alcohol, pyridine, and glacial acetic acid. The rotatory power of the isomeric nitrobenzobornylamides in the last three solvents was investigated at various temperatures, ranging from 20° to about 45°, but in the case of the benzo- and toluobornylamides the rotations at only one temperature, namely, 20°, were observed. Determinations of the molecular solution volumes of the nitrobenzobornylamides in the same solvents have also been made.

The more important values obtained for these compounds are given below:

o-Nitrobenzobornylamide.

Solvent.	<i>p</i> .	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.	Mol. sol. vol.
Ethyl alcohol	4·9799	- 22·39°	- 67·62°	—
Methyl alcohol	5·0654	30·32	91·57	246·1 c.c.
Glacial acetic acid	3·9454	13·54	40·89	250·9 „
Pyridine	5·0011	5·88	17·76	250·4 „
„	10·0870	7·67	23·16	255·0 „

m-Nitrobenzobornylamide.

Solvent.	<i>p</i> .	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.	Mol. sol. vol.
Ethyl alcohol	2·6399	- 27·91°	- 84·29°	—
Methyl alcohol	1·9190	- 24·62	- 74·35	241·0 c.c.
Glacial acetic acid	3·8987	- 12·16	- 36·72	251·0 „
Pyridine	5·0079	+ 27·22	+ 82·20	250·5 „
„	9·9862	+ 22·16	+ 66·92	252·5 „

p-Nitrobenzobornylamide.

Solvent.	<i>p</i> .	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.	Mol. sol. vol.
Ethyl alcohol	4·2770	- 16·75°	- 50·58°	—
Methyl alcohol	5·0035	- 13·44	- 40·59	247·5 c.c.
Glacial acetic acid	3·8347	- 7·28	- 21·98	251·2 „
Pyridine	4·7106	+ 26·41	+ 79·76	250·1 „
„	9·9493	+ 22·80	+ 68·86	252·1 „

Solvent.	Benzobornylamide.		Toluobornylamides.			
	[M] _D ^{20°} .		[M] _D ^{20°} .			
	<i>p</i> (approx.).		<i>p</i> (approx.).	Ortho-.	Meta-.	Para-.
Ethyl alcohol.....	5	-58·93°	2·5	-50·24°	-57·75°	-36·23°
" " ".....	10	-62·63	5·0	-51·60	-60·70	-39·43
Methyl alcohol ...	5	-57·44	2·0	-46·12	-55·20	-33·01
" " ".....	10	-59·88	4·0	-46·10	-58·54	-33·90
Glacial acetic acid	5	-26·14	5·0	-28·13	-22·09	-1·33
" " ".....	10	-29·94	10·0	-30·73	-24·34	-4·09
Pyridine	5	+66·67	5·0	+30·38	+72·90	+82·93
" " ".....	10	+59·06	10·0	+27·75	+62·45	+74·23

It will be observed that the rotatory power of the bornylamides of these aromatic acids is influenced by the nature of the solvent and the concentration in a similar manner to that of the aliphatic bornylamides already described in the previous communication. It was pointed out, in dealing with the latter compounds, that they were of very much lower negative rotation in pyridine than in methyl-alcoholic solution. This is again found to be true for the aromatic bornylamides; but, owing to the greater effect of the solvent, the change from methyl alcohol to pyridine is accompanied in all these compounds, with the exception of *o*-nitrobenzobornylamide, by a complete reversal in the sign of the rotation—the rotatory power in the former solvent being negative, and in the latter positive. It will also be observed that the rotatory powers preserve the same order in the different solvents as in the case of the aliphatic bornylamides, the values in acetic acid solution lying between those in pyridine and methyl-alcoholic solution.

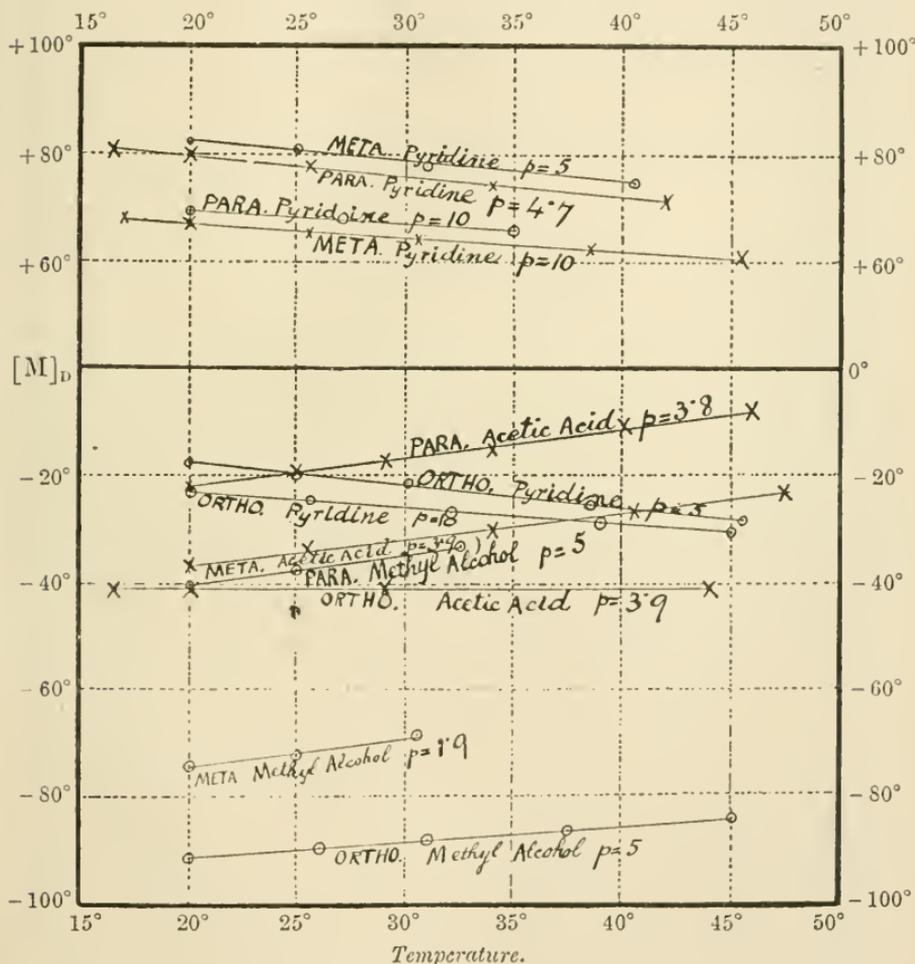
The rotatory power of the aromatic bornylamides is affected by the concentration in a similar manner to the other acyl-bornylamides, the rotations becoming greater, in a negative sense, as the concentration increases. Bearing on this variation in the rotatory power with the concentration, it is worthy of note that in glacial acetic acid solution of concentration $p=10$, *p*-toluobornylamide has a molecular rotation of $-4\cdot09$, whilst in one per cent. glacial acetic acid solution it is completely inactive.

Turning to the influence of temperature on the rotation of the nitrobenzobornylamides, it is found that as a general rule increase in this factor results in a diminution of rotatory power, as may readily be seen from the accompanying diagram.

It will only be necessary here to indicate the following points. Firstly, in pyridine solution, the rotatory powers of the three nitrobenzobornylamides diminish in a positive sense at about the same rate. This, of course, necessitates that the levorotation of the ortho-compound increases with rise of temperature. Secondly, the negative rotations in methyl-alcoholic solution also diminish as the

temperature increases. Thirdly, whilst the lævorotation of the meta- and para-nitrobenzobornylamides in glacial acetic acid solution decreases uniformly as the temperature rises, that of the ortho-isomeride is scarcely affected, the rotation at 16.5° being practically identical with the value found at 44°.

Molecular rotation of the nitrobenzobornylamides in pyridine, methyl alcohol, and acetic acid solution.



N.B.—In order to shorten the diagram the ordinates from 0° to +40° have been omitted.

In several respects the *o*-nitrobenzo-compound is abnormal in its behaviour. In the first place, the rotatory powers in pyridine are negative, whilst those of the corresponding meta- and para-compounds are positive. Further, it is strongly marked off from the isomeric nitrobenzobornylamides in possessing a lower lævo-

rotation in ethyl alcohol than in methyl-alcoholic solution. It also differs from the isomeric compounds by showing, as we have just seen, practically no variation of rotatory power with increase of temperature in glacial acetic acid solution.

In connexion with this abnormality in the optical behaviour of *o*-nitrobenzobornylamide, it is worthy of note that, of the three isomerides, this has the highest melting point, and thus exhibits the exceptional phenomenon of an ortho-compound melting at a higher temperature than the corresponding para-derivative.

The only active compounds containing the three isomeric nitrobenzo-groups which have up to the present been investigated are the nitrobenzoyl-*d*-carvoximes, the methyl and ethyl esters of the dinitrobenzoyltartaric acids, and the menthyl nitrobenzoates; and in these cases also, the ortho-compounds show an abnormal behaviour as compared with the meta- and para-isomerides. The rotations obtained for these compounds have been collected in the tables given on pp. 2033, 2034.

From the values there given, it will be observed that, with the nitrobenzoyl-*d*-carvoximes, this abnormality of the ortho-compound manifests itself in the complete absence of rotatory power, although, from analogy to other position-isomeric active compounds, it would be anticipated that, in this case, the ortho-derivative should have the highest dextrorotation of the three. The inactivity cannot be explained by racemisation, since, on hydrolysis, a dextrorotatory and not an inactive carvoxime was obtained. The rotation of the *o*-nitrobenzoyl compound appears, however, to have been investigated at two concentrations, which did not differ materially from one another; and, just as *p*-toluobornylamide in glacial acetic acid solution at a particular concentration and temperature was found by us to be inactive, so the exceptional value found by Goldschmidt and Freund for the rotation of *o*-nitrobenzoyl-*d*-carvoxime may be due to its having been examined in such a solvent, and under such conditions of temperature and concentration that the activity of the compound was completely suppressed. It is, moreover, worthy of note that the authors mention that at the temperature of solid carbon dioxide the chloroform solution did exhibit a very feeble rotation.

In the case of the ethyl dinitrobenzoyltartrates (P. F. Frankland and Harger, *Trans.*, 1904, **85**, 1571), the rotation of the ortho-compound has such a very large temperature-coefficient that, at high temperatures, it is less, and at low temperatures greater, than the rotation of its isomerides, and the same appears to be also the case for the methyl ester (P. F. Frankland and Harger, *loc. cit.*), concerning which, however, the data are not so complete.

The isomeric menthyl nitrobenzoates of Cohen and Armes (Trans., 1905, **87**, 1190) also show the ortho-compound to possess certain exceptional features with regard to its rotation, more especially in the magnitude of its temperature-coefficient.

It was thought that this difference in the behaviour of the ortho-compound might be due to its possessing a different constitution from the meta- and para-compounds, and, with the view of testing this supposition, we made a large number of observations on the refractive power of the nitrobenzobornylamides in solution, which, however, failed to throw any light on this point. The molecular refraction of these compounds varies with the solvent in very much the same manner for each, ortho-nitrobenzobornylamide showing no marked difference from the meta- and para-isomerides.

It has been pointed out from theoretical considerations (Frankland and Wharton, Trans., 1896, **69**, 1309, 1583) that, in the case of isomeric di-substituted benzene rings, the para-isomeride should exert the greatest influence on the rotation, and the ortho the least, whilst the influence of the meta-isomeride should be intermediate between that exerted by the ortho- and para-compounds respectively; it has, however, also been shown that the methyl and ethyl dinitrobenzoyltartrates (P. F. Frankland and Harger, *loc. cit.*) give exceptional values for the ortho-compound, and similar exceptional results have been obtained in the case of the nitrobenzoyl-*d*-carboximes (Goldschmidt and Freund, *loc. cit.*), the β -methyladipotoluidides (Rawitzer, *Thesis*, Zürich, 1896, 25; Guye, *Bull. Soc. chim.*, 1896, [iii], **15**, 1158), and more recently in that of the hydroxy- and methoxy-benzylidenecamphors (Haller, *Compt. rend.*, 1891, **113**, 22; Haller and Müller, *ibid.*, 1899, **128**, 1370; Haller and Bauer, *ibid.*, 1909, **148**, 1490).

The observations which we have made on the rotatory powers of the nitrobenzo- and toluo-bornylamides do not, however, support the general rule. It will be seen, on reference to the tables given on pp. 2036 and 2042, that the relationship between the rotatory effects of position-isomeric groups depends to a very great extent on the solvent in which the compounds are examined.

Of the isomeric nitrobenzobornylamides, the ortho-compound has in all solvents a greater lævorotation than the para-isomeride, but *m*-nitrobenzobornylamide occupies every possible position with respect to the isomeric compounds. Thus, in methyl and glacial acetic acid solutions, as well as in pyridine solution of concentration $p=10$, the rotations of the nitrobenzobornylamides exhibit the usual order, namely, ortho, meta, para; in ethyl-alcoholic solution, the order of the rotatory effects is meta, ortho, para; whilst in pyridine

solution of concentration $p=5$, the rotations show the order, ortho, para, meta.

The rotatory effects of the toluoyl groups are, on the whole, not so erratic as those of the nitrobenzoyl groups. In both glacial acetic acid and pyridine solutions, the rotations of the toluobornyl-amides stand in the order predicted from theoretical considerations, but in methyl- and ethyl-alcoholic solutions the rotatory power of the ortho-isomeride is intermediate between those of the meta- and para-compounds respectively.

The molecular rotations of the nitrobenzo- and toluo-bornyl-amides enable us to compare the rotatory effect of the methyl and nitro-groups when substituted in the ortho-, meta-, and para-positions of the benzene ring respectively. The comparison is, however, rendered difficult owing to the large variations in the rotations induced by solvents.

Introduction of the nitro-group in the para-position of the benzene ring exerts, in all solvents, a dextrorotatory influence on the rotation of benzobornylamide; a similar but more pronounced effect is also produced by the para-methyl group. Substitution with the nitro-group in the ortho-position exerts a lævorotatory influence in all solvents employed, and the same is also true in the case of the methyl group in acetic acid and pyridine solutions; in methyl- and ethyl-alcoholic solutions, on the other hand, the introduction of the methyl group in the ortho-position is accompanied by a dextro-rotatory influence.

In the meta-position, introduction of the methyl group produces comparatively little influence on the rotation of benzobornylamide, whereas the nitro-group in the same position exerts, in all solvents with the exception of pyridine, a marked lævorotatory influence.

The influence of the methyl and nitro-groups on the rotation of benzobornylamide may be readily compared by means of the following table, in which their rotatory effects in the various positions of the benzene ring are contrasted:

Influence of Methyl and Nitro-groups on the Molecular Rotation, $[M]_D^{20}$, of Benzobornylamide.

Solvent.	Ortho.		Meta.		Para.	
	CH ₃ .	NO ₂ .	CH ₃ .	NO ₂ .	CH ₃ .	NO ₂ .
Ethyl alcohol	+7·3°	-8·7°	-1·8°	-25·4°	+19·5°	+8·3°
Methyl alcohol ...	+11·3	-34·1	-1·1	-16·9	+23·5	+16·8
Glacial acetic acid	-2·0	-14·7	+4·0	-10·5	+24·8	+4·2
Pyridine, $p=5$...	-36·3	-84·4	+6·2	+15·6	+16·3	+13·1
„ $p=10$...	-31·3	-82·2	+2·9	+7·9	+15·2	+9·8

In connexion with the rotatory effect of the methyl and nitro-groups, the above results may be compared with those obtained in

other series by means of the tables given below, in which the data so far available for effecting a comparison of the rotatory influences of the two groups in all three positions of the benzene ring have been collected:

*Acyl-d-carvoximes.**

Rotation in Chloroform Solution.

	<i>p.</i>	<i>t</i> °.	[M] _D ^c .		<i>p.</i>	<i>t</i> °.	[M] _D ^c .
<i>o</i> -Nitrobenzoyl	4·7044	20·0°	0·00°	Benzoyl	9·1058	18·5	+71·66°
„	4·5575	„	0·00	<i>o</i> -Tolnoyl	9·1942	15·5	+76·64
<i>m</i> -Nitrobenzoyl	4·5845	23·5	+64·94	<i>m</i> -Tolnoyl	10·0169	15·5	+76·01
<i>p</i> -Nitrobenzoyl	4·5648	22·5	+54·42	<i>p</i> -Tolnoyl	9·2950	15·5	+66·34

* Goldschmidt and Freund (*Zeitsch. physikal. Chem.*, 1894, **14**, 394).

Diethyldiacyltartrates.

<i>t</i> °.	Ethyl dibenzoyl-tartrate.*	Ethyl dinitrobenzoyltartrates.†			Ethyl ditolnoyltartrates.‡		
		[M] _D ^c .			[M] _D ^c .		
		Ortho.	Meta.	Para.	Ortho.	Meta.	Para.
20°	-247·0°	-651·2°	-357·3°	-638·9°	-266·8°	-306·0°	—
100	251·6	315·8	324·3	490·0	241·9	381·7	-397·7°
135	235·5	214·9	298·4	430·8	222·6	281·7	362·0
180	215·0	117·3	248·5	340·1	—	—	311·0

* Frankland and Wharton, *Trans.*, 1896, **69**, 1583.

† Frankland and Harger, *Trans.*, 1904, **85**, 1571.

‡ Frankland and Wharton, *Trans.*, 1896, **69**, 1309.

Dimethyldiacyltartrates.

<i>t</i> °.	Methyl dibenzoyl-tartrate.*	Methyl dinitrobenzoyltartrates.†			Methyl ditolnoyltartrates.‡		
		[M] _D ^c .			[M] _D ^c .		
		Ortho.	Meta.	Para.	Ortho.	Meta.	Para.
20°	—	—	-379·1°	—	-324·3°	—	—
100	-280·1°	[-466·3°]§	329·5	-512·0°	282·3	-327·1°	-425·7°
135	259·2	[429·9]§	296·4	444·3	255·0	293·1	378·9
180	225·5	[<i>t</i> =109°]	—	253·5	363·4	220·8	254·9
							322·2

* Frankland and Wharton, *loc. cit.*

† Frankland and Harger, *loc. cit.*

‡ Frankland and Wharton, *loc. cit.*

§ The values enclosed in brackets are only approximate, for no density determinations of dimethyl di-*o*-nitrobenzoyltartrate were made, the corresponding densities of the meta-compound having been used for the approximate calculation of the molecular rotation.

Menthyl Esters.

t° .	Menthyl nitrobenzoates, $[M]_D^{20^\circ}$ *			Menthyl- Benzoate †.....	t° .	$[M]_D$.
	Ortho.	Meta.	Para.			
100°	-370.0°	-250.3°	-230.0°	20° ‡	-263.3° §	
80	380.6	253.4	232.2	<i>o</i> -Toluate †	20	231.3
70	379.3	252.2	233.5	<i>m</i> -Toluate †	20	241.0
65	380.1	251.1	234.7	<i>p</i> -Toluate †	20	252.5 §
20	—	252.2	—			

* Cohen and Armes, *Trans.*, 1905, **87**, 1190.

† Tschugaeff, *Ber.*, 1898, **31**, 1775.

‡ The temperature of observation was presumably 20° in each case, as the density is given for that temperature for the *o*- and *m*-compounds.

§ Rotation in benzene solution, all the other values being for the liquid state.

The comparison of the rotatory effects of the methyl and nitro-groups may also be instituted by means of the three tartaroditoluidides and the three nitroanilides respectively. The tartarodinitroanilides have been prepared and polarimetrically examined by one of us in conjunction with Miss M. B. Thomas, and the results, a summary of which is given below, will form the subject of a future communication.

Rotation in Pyridine Solution.

	p .	$[M]_D^{20^\circ}$.		p .	$[M]_D^{20^\circ}$.
Tartarodianilide *	{	1.820			+737
		5.421			+740
Tartarodi-	p .	$[M]_D^{20^\circ}$.	Tartarodi-	p .	$[M]_D^{20^\circ}$.
<i>o</i> -Nitroanilide	2.676	+375°	<i>o</i> -Toluidide *	3.012	+653°
„	2.894	375	„	4.994	667
<i>m</i> -Nitroanilide	2.197	768	<i>m</i> -Toluidide *	2.153	710
„	3.261	764	„	6.65	713
<i>p</i> -Nitroanilide	1.688	1072	<i>p</i> -Toluidide *	3.885	790
„	2.158	1069	„	4.502	790

* Frankland and Slator, *Trans.*, 1903, **83**, 1349.

EXPERIMENTAL

Benzobornylamide.

Twelve grams of bornylamine hydrochloride were dissolved in water, and the free bornylamine precipitated by the addition of an excess of a dilute aqueous solution of potassium hydroxide. The amine was dissolved by the addition of ether, and a little more than the calculated amount of benzoyl chloride in ethereal solution slowly run in, the mixture being well agitated in order to decompose the bornylamine hydrochloride formed in the reaction. On

evaporation of the ethereal solution, benzobornylamide is left behind in small, colourless needles, which, on recrystallisation from dilute alcohol, melt at 138.5°. It is readily soluble in pyridine, acetic acid, or alcohol:

0.3020 gave 14.3 c.c. N₂ (moist) at 14° and 759 mm. N = 5.56.
C₁₇H₂₃ON requires N = 5.45 per cent.

Rotatory Power of Benzobornylamide.

p. *d* 20°/4°. *l* in mm. $\alpha_D^{20^\circ}$. $[\alpha]_D^{20^\circ}$. $[M]_D^{20^\circ}$.

Ethyl-Alcoholic Solution.

4.9940	0.8017	389.9	-3.58°	-22.93°	-58.93°
9.9747	0.8128	199.84	3.95	24.37	62.63

Methyl-Alcoholic Solution.

5.0013	0.8054	389.9	-3.51°	-22.35°	-57.44°
10.0079	0.8177	199.84	3.81	23.30	59.88

Glacial Acetic Acid Solution.

5.0055	1.0535	389.9	-2.09°	-10.17°	-26.14°
10.0524	1.0550	199.84	2.47	11.65	29.94

Pyridine Solution.

5.0151	0.9817	389.9	+4.98°	+25.94°	+66.67°
9.9567	0.9864	199.84	4.51	22.98	59.06

The value given above for the rotatory power in ethyl-alcoholic solution is slightly greater than that found by Forster, namely, $[\alpha]_D^{20^\circ} - 21.8^\circ$, $c = 4.0052$.

o-Nitrobenzobornylamide.

This was prepared from 12 grams of bornylamine and the theoretical amount of *o*-nitrobenzoyl chloride in ethereal solution (150—200 c.c.), in a similar manner to that employed in the case of the benzo-derivative. After some time, the greater part of the amide crystallises out, whilst from the ethereal solution the remainder is obtained on evaporation. It was recrystallised from dilute alcohol until of constant rotatory power:

0.1459 gave 12.0 c.c. N₂ (moist) at 13.0° and 737.5 mm. N = 9.41.
C₁₇H₂₂O₃N₂ requires N = 9.27 per cent.

o-Nitrobenzobornylamide crystallises in colourless, prismatic needles, melting at 173°. It is readily soluble in pyridine or chloroform, moderately so in alcohol, and less soluble in ether.

*Rotatory Power of o-Nitrobenzobornylamide.**Ethyl-Alcoholic Solution.*

<i>p.</i>	Density 20°/4°.	α_D^{20} <i>l</i> = 389.9 mm.	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
4.9799	0.8049	-3.50°	-22.39°	-67.62°

Methyl-Alcoholic Solution, p = 5.0654.

Temperature.	Density <i>t</i> °/4°.	α_D <i>l</i> = 389.9 mm.	$[\alpha]_D^t$.	$[M]_D^t$.
20.0°	0.8067	-4.83°	-30.32°	-91.57°
26.0	0.8012	4.70	29.70	89.69
31.0	0.7965	4.59	29.18	88.12
37.5	0.7903	4.47	28.64	86.49
45.0	0.7831	4.31	27.87	84.16

Densities determined :

Temperature.....	20°	25°	35°	45°
Density <i>t</i> °/4°.....	0.8067	0.8020	0.7928	0.7831

Glacial Acetic Acid Solution, p = 3.9454.

Temperature.	Density <i>t</i> °/4°.	α_D^t <i>l</i> = 389.9 mm.	$[\alpha]_D^t$.	$[M]_D^t$.
16.5°	1.0598	-2.24°	-13.74°	-41.49°
20.0	1.0565	2.20	13.54	40.89
29.0	1.0466	2.18	13.54	40.89
44.0	1.0300	2.14	13.51	40.80

Densities determined :

Temperature.....	20°	25°	35°
Density <i>t</i> °/4°.....	1.0565	1.0511	1.0400

Pyridine Solution, p = 5.0011.

Temperature.	Density <i>t</i> °/4°.	α_D^t <i>l</i> = 389.9 mm.	$[\alpha]_D^t$.	$[M]_D^t$.
20.0°	0.9860	-1.13°	-5.88°	-17.76°
25.0	0.9810	1.24	6.48	19.57
30.0	0.9760	1.35	7.09	21.41
38.5	0.9678	1.60	8.48	25.61
45.5	0.9608	1.78	9.50	28.69

Densities determined :

Temperature.....	20°	25°	35°	45°
Density <i>t</i> °/4°.....	0.9860	0.9810	0.9713	0.9613

Pyridine Solution, $p=10.087$.

Temperature.	Density $t^{\circ}/4^{\circ}$.	$\alpha_D^{t^{\circ}}$ $l=389.9$ mm.	$[\alpha]_D^{t^{\circ}}$.	$[M]_D^{t^{\circ}}$.
20.0°	0.9949	-3.00°	-7.67°	-23.16°
25.5	0.9896	3.22	8.27	24.97
32.0	0.9836	3.45	8.92	26.94
39.0	0.9766	3.62	9.43	28.48
45.0	0.9707	3.78	9.90	29.90

Densities determined:

Temperature	20°	25°	35°	45°
Density $t^{\circ}/4^{\circ}$	0.9949	0.9901	0.9806	0.9707

m-Nitrobenzobornylamide.

The preparation of this compound was accomplished by the interaction of bornylamine (12 grams) and the theoretical amount of *m*-nitrobenzoyl chloride in ethereal solution (150 c.c.), in exactly the same way as that described for the benzo-compound. The greater portion of the amide crystallised out from the ethereal solution after some time. Purification was effected by recrystallisation from dilute alcohol:

0.1423 gave 11.6 c.c. N_2 (moist) at 15° and 746.5 mm. $N=9.36$.

$C_{17}H_{22}O_3N_2$ requires $N=9.27$ per cent.

m-Nitrobenzobornylamide crystallises in almost colourless needles, melting at 161° without decomposition. Its solubility in the ordinary solvents is less than that of the corresponding ortho- and para-compounds.

*Rotatory Power of m-Nitrobenzobornylamide.**Ethyl-Alcoholic Solution.*

p .	Density $20^{\circ}/4^{\circ}$.	$\alpha_D^{20^{\circ}}$ $l=389.9$ mm.	$[\alpha]_D^{20^{\circ}}$.	$[M]_D^{20^{\circ}}$.
2.6399	0.7972	-2.29°	-27.91°	-84.29°

Methyl-Alcoholic Solution, $p=1.9190$.

Temperature.	Density $t^{\circ}/4^{\circ}$.	$\alpha_D^{t^{\circ}}$ $l=389.9$ mm.	$[\alpha]_D^{t^{\circ}}$.	$[M]_D^{t^{\circ}}$.
20.0°	0.7979	-1.47°	-24.62°	-74.35°
25.0	0.7930	1.44	24.27	73.29
30.5	0.7880	1.34	22.73	68.64

Densities determined:

Temperature	20°	25°	35°
Density $t^{\circ}/4^{\circ}$	0.7979	0.7930	0.7838

Glacial Acetic Acid Solution, $p = 3.8987$.

Temperature.	Density $t^{\circ}/4^{\circ}$.	α_D^t $l = 389.9$ mm.	$[\alpha]_D^t$.	$[M]_D^t$.
20.0°	1.0548	-1.95°	-12.16°	-36.72°
25.5	1.0505	1.78	11.15	33.67
31.0	1.0408	1.58	9.99	30.17
40.5	1.0335	1.38	8.78	26.52
47.5	1.0256	1.20	7.70	23.25

Densities determined:

Temperature	20°	25°	35°	45°
Density $t^{\circ}/4^{\circ}$	1.0548	1.0509	1.0398	1.0286

Pyridine Solution, $p = 5.0079$.

Temperature.	Density $t^{\circ}/4^{\circ}$.	α_D^t $l = 389.9$ mm.	$[\alpha]_D^t$.	$[M]_D^t$.
20.0°	0.9860	+5.24°	+27.22°	+82.20°
25.0	0.9811	5.16	26.94	81.36
31.0	0.9751	4.94	25.95	78.47
40.5	0.9658	4.66	24.71	74.62

Densities determined:

Temperature	20°	25°	35°	45°
Density $t^{\circ}/4^{\circ}$	0.9860	0.9811	0.9713	0.9613

Pyridine Solution, $p = 9.9862$.

Temperature.	Density $t^{\circ}/4^{\circ}$.	α_D^t $l = 199.84$ mm.	$[\alpha]_D^t$.	$[M]_D^t$.
17.0°	0.9978	+4.50°	+22.60°	+68.25°
20.0	0.9948	4.40	22.16	66.92
25.5	0.9897	4.27	21.62	65.29
30.5	0.9848	4.17	21.22	64.08
38.5	0.9771	4.00	20.51	61.94
45.5	0.9702	3.88	20.04	60.52

Densities determined:

Temperature	20°	25°	35°	45°
Density $t^{\circ}/4^{\circ}$	0.9948	0.9901	0.9805	0.9707

p-Nitrobenzobornylamide.

The method of preparation was the same as that employed in the case of the preceding compounds, enough ether being used to keep the whole of the amide in solution. The product obtained by evaporating the ethereal solution was purified by recrystallising from dilute alcohol:

0.1452 gave 11.6 c.c. N_2 (moist) at 14° and 756 mm. $N = 9.35$.

$C_{17}H_{22}O_3N_2$ requires $N = 9.27$ per cent.

p-Nitrobenzobornylamide crystallises in long, slender needles of

a pale yellow colour, melting at 167°. It is readily soluble in pyridine, and moderately so in alcohol or acetic acid.

Rotatory Power of p-Nitrobenzobornylamide.

Ethyl-Alcoholic Solution.

<i>p.</i>	Density 20°/4°.	$\alpha_D^{20^\circ}$ <i>l</i> = 389.9 mm.	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.
4.1933	0.8017	-2.17°	-16.56°	-50.01°
4.2770	0.8020	2.24	16.75	50.58

Methyl-Alcoholic Solution, p = 5.0035.

Temperature.	Density <i>t</i> °/4°.	α_D^t <i>l</i> = 389.9 mm.	$[\alpha]_D^t$.	$[M]_D^t$.
20.0°	0.8085	-2.12°	-13.44°	-40.59°
25.0	0.8040	1.96	12.49	37.72
35.0	0.7951	1.70	10.96	33.10

Densities determined:

Temperature.....	20°	25°	35°
Density <i>t</i> °/4°.....	0.8085	0.8040	0.7951

Glacial Acetic Acid Solution, p = 3.8347.

Temperature.	Density <i>t</i> °/4°.	α_D^t <i>l</i> = 389.9 mm.	$[\alpha]_D^t$.	$[M]_D^t$.
20°	1.0565	-1.15°	-7.28°	-21.98°
25	1.0512	1.03	6.55	19.78
29	1.0465	0.90	5.76	17.39
34	1.0410	0.78	5.01	15.13
40	1.0343	0.58	3.75	11.32
46	1.0274	0.42	2.74	8.28

Densities determined:

Temperature.....	20°	35°	45°
Density <i>t</i> °/4°.....	1.0565	1.0397	1.0286

Pyridine Solution, p = 4.7106.

Temperature.	Density <i>t</i> °/4°.	α_D^t <i>l</i> = 389.9 mm.	$[\alpha]_D^t$.	$[M]_D^t$.
16.5°	0.9888	+4.85°	+26.71°	+80.66°
20.0	0.9855	4.78	26.41	79.76
25.5	0.9801	4.63	25.71	77.64
34.0	0.9717	4.36	24.45	73.84
42.0	0.9638	4.18	23.61	71.30

Densities determined:

Temperature	20°	25°	35°	45°
Density <i>t</i> °/4°	0.9855	0.9806	0.9708	0.9609

Pyridine Solution, $\rho = 9.9493$.

Temperature.	Density $t^{\circ}/4^{\circ}$.	α_D^t $l = 199.84$ mm.	$[\alpha]_D^t$.	$[M]_D^t$.
20°	0.9949	+4.51°	+22.80°	+68.86°
27	0.9881	4.42	22.50	67.95
35	0.9804	4.23	21.70	65.53

Densities determined:

Temperature.....	20°	25°	35°
Density $t^{\circ}/4^{\circ}$	0.9949	0.9902	0.9804

o-Toluobornylamide.

The mode of preparation was similar to that adopted in the case of the nitrobenzo-compounds. The product left after distilling off the ether was crystallised from a mixture of benzene and light petroleum until of constant rotatory power:

0.2963 gave 13.1 c.c. N_2 (moist) at 9° and 756 mm. $N = 5.28$.

$C_{18}H_{25}ON$ requires $N = 5.17$ per cent.

o-Toluobornylamide crystallises in colourless needles, melting at 97—98°. It is readily soluble in benzene, acetone, or pyridine, and only slightly soluble in light petroleum.

Rotatory Power of o-Toluobornylamide.

p .	$d, 20^{\circ}/4^{\circ}$.	l in mm.	$\alpha_D^{20^{\circ}}$.	$[\alpha]_D^{20^{\circ}}$.	$[M]_D^{20^{\circ}}$.
-------	-----------------------------	------------	---------------------------	-----------------------------	------------------------

Ethyl-Alcoholic Solution.

2.5037	0.7956	389.9	-1.44°	-18.54°	-50.24°
5.0002	0.7999	389.9	-2.97	-19.04	-51.60

Methyl-Alcoholic Solution.

1.9986	0.7991	389.9	-1.06	-17.02	-46.12
4.0052	0.8016	389.9	-2.13	-17.01	-46.10

Glacial Acetic Acid Solution.

5.0307	1.0508	389.9	-2.14	-10.38	-28.13
9.9783	1.0521	199.84	-2.38	-11.34	-30.73

Pyridine Solution.

4.9955	0.9804	389.9	+2.14	+11.21	+30.38
9.9977	0.9845	389.9	+3.93	+10.24	+27.75

m-Toluobornylamide.

This was prepared in the usual manner by the interaction of the acid chloride and bornylamine in ethereal solution, and purified by crystallisation from dilute alcohol:

0.2954 gave 13.2 c.c. N_2 (moist) at 14.5° and 756 mm. $N=5.20$.

$C_{18}H_{25}ON$ requires $N=5.17$ per cent.

m-Toluobornylamide crystallises in fine, silky needles, melting at $140-141^\circ$. It is easily soluble in pyridine or glacial acetic acid, and moderately so in alcohol.

Rotatory Power of m-Toluobornylamide.

<i>p.</i>	<i>d.</i> $20^\circ/4^\circ$.	<i>l</i> in mm.	$\alpha_D^{20^\circ}$.	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.
-----------	--------------------------------	-----------------	-------------------------	---------------------------	----------------------

Ethyl-Alcoholic Solution.

2.5032	0.7932	389.9	-1.65°	-21.31°	-57.75°
5.0073	0.8003	389.9	-3.50	-22.40	-60.70

Methyl-Alcoholic Solution.

2.0004	0.7994	389.9	-1.27	-20.37	-55.20
4.0056	0.8033	389.9	-2.71	-21.60	-58.54

Glacial Acetic Acid Solution.

5.0038	1.0506	389.9	-1.67	-8.15	-22.09
10.0215	1.0513	199.84	-1.89	-8.98	-24.34

Pyridine Solution.

4.9922	0.9816	389.9	+5.14	+26.90	+72.90
10.0080	0.9850	199.84	+4.54	+28.05	+62.45

p-Toluobornylamide.

This was prepared from *p*-toluoyl chloride and bornylamine in the same manner as that employed in the case of the preceding compounds. On evaporating the ether, a theoretical yield of the amide was obtained. It was purified by recrystallising from dilute alcohol until of constant rotatory power:

0.3043 gave 14.0 c.c. N_2 (moist) at 13° and 741 mm. $N=5.29$.

$C_{18}H_{25}ON$ requires $N=5.17$ per cent.

p-Toluobornylamide crystallises in colourless, prismatic needles, melting at 169° without decomposition. Like the isomeric amides described above, it is readily soluble in pyridine or glacial acetic acid. At the ordinary temperature it gives only about a 4 per cent. solution in methyl alcohol.

Rotatory Power of p-Toluobornylamide.

<i>p.</i>	<i>d.</i> 20°/4°.	<i>l</i> in mm.	$\alpha_D^{20^\circ}$.	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.
<i>Ethyl-Alcoholic Solution.</i>					
2.4839	0.7956	389.9	-1.03°	-13.37°	-36.23°
5.0187	0.8010	389.9	-2.28	-14.55	-39.43
<i>Methyl-Alcoholic Solution.</i>					
2.0026	0.7989	389.9	-0.76	-12.18	-33.01
4.0036	0.8038	389.9	-1.57	-12.51	-33.90
<i>Glacial Acetic Acid Solution.</i>					
1.0010	1.0501	389.9	±0.0	±0.0	±0.0
5.0022	1.0508	389.9	-0.10	-0.49	-1.33
10.0130	1.0519	389.9	-0.62	-1.51	-4.09
<i>Pyridine Solution.</i>					
5.0064	0.9810	389.9	+5.86	+30.60	+82.93
7.9820	0.9835	389.9	+8.83	+29.03	+78.67
16.0225	0.9842	199.84	+5.40	+27.39	+74.23

UNIVERSITY,
BIRMINGHAM.

CCXXIII.—*Ethyl Benzoylacetate.*

By EDWARD HOPE and WILLIAM HENRY PERKIN, jun.

ETHYL benzoylacetate was discovered by Baeyer in 1882 (*Ber.*, 15, 2705), and the first investigations of this important substance and of many of its derivatives are described in several papers published between this date and 1886.* The ester had, at that time, to be prepared by the action of concentrated sulphuric acid on ethyl phenylpropionate, a process which not only yielded an impure product, but was at the same time so laborious that experimental investigation could only be carried out with very small quantities of material. Ethyl benzoylacetate is now a commercial substance, and, during the course of some recent experiments with the pure ester, we were led to the conclusion that some of the statements in the original papers, made more especially in connexion with the substitution derivatives, were incorrect, and that others required modification. Ethyl benzoyl-

* Baeyer and Perkin (*Ber.*, 1883, 16, 2128); Perkin (*Trans.*, 1884, 45, 170; 1885, 47, 240, 262); Perkin and Calman (*Trans.*, 1886, 49, 154); Perkin and Bellencot (*Trans.*, 1886, 49, 440).

acetate is readily converted into such mono-substitution products as ethyl α -benzoylpropionate, $C_6H_5 \cdot CO \cdot CHMe \cdot CO_2Et$, and ethyl α -benzoylbutyrate, $C_6H_5 \cdot CO \cdot CHEt \cdot CO_2Et$, by treatment, in alcoholic solution, with sodium ethoxide and the alkyl iodide, the process being exactly similar to that commonly employed in preparing substitution derivatives of ethyl acetoacetate.

Disubstitution derivatives of ethyl benzoylacetate, such as ethyl α -benzoyl*isobutyrate*, $C_6H_5 \cdot CO \cdot CMe_2 \cdot CO_2Et$, and ethyl α -benzoyl- α -ethylbutyrate, $C_6H_5 \cdot CO \cdot CEt_2 \cdot CO_2Et$, unlike those of ethyl acetoacetate, can either not be prepared at all, or only in very small yields, by treating the mono-substituted ester with sodium ethoxide and the alkyl iodide in alcoholic solution. On the other hand, such disubstitution derivatives may be obtained in the absence of alcohol, namely, by acting, for example, on the toluene solution of the mono-substitution derivative, first with sodium, and then with the alkyl iodide. Under these conditions, ethyl α -benzoyl-*isobutyrate* is obtained in a yield of at least 60 per cent. of that theoretically possible (p. 2046), but, on the other hand, it is remarkable that the introduction of the second ethyl group into ethyl α -benzoylbutyrate takes place with much more difficulty, and the yield of disubstitution derivative does not, as far as can be judged, exceed 20 per cent. of that theoretically possible.

There can be no doubt that the explanation of this discrepancy is to be sought in the greater reactivity of methyl iodide, and, in support of this view, we find that the yield of ethyl α -benzoyl- α -methylbutyrate, $C_6H_5 \cdot CO \cdot CMeEt \cdot CO_2Et$, is greater when methyl iodide reacts in toluene solution with the sodium derivative of ethyl α -benzoylbutyrate than when ethyl iodide reacts with the sodium derivative of ethyl α -benzoylpropionate. Again, it is well known that benzyl chloride is very reactive, and, in accordance with the above explanation, we find that the sodium derivative of ethyl α -benzoylbutyrate reacts readily with benzyl chloride, and the yield of ethyl α -benzoyl- β -phenyl- α -ethylpropionate,



obtained is at least 60 per cent. of that theoretically possible.

These results are at variance with the earlier work of Perkin (Trans., 1884, 45, 182), in which it is stated that ethyl benzoyl-diethylacetate (ethyl α -benzoyl- α -ethylbutyrate) is produced when ethyl benzoylethylacetate (ethyl α -benzoylbutyrate) is treated with sodium ethoxide and ethyl iodide in alcoholic solution. The product was not purified by fractional distillation, but the disubstitution derivative must have been formed, because the ester yielded diethylacetophenone on hydrolysis; unfortunately, there is no record of the amount of this latter substance which was

obtained. Discrepancies such as this, which one of the authors (P) and others have repeatedly noticed, especially in cases of this kind, must be due to slight differences in the conditions of experiment, and very probably to the presence or absence of varying quantities of moisture in the alcohol and other materials employed. The second point, which we have carefully investigated and deal with in detail in the present communication, is the behaviour of the substitution derivatives of ethyl benzoylacetate on hydrolysis. It was early recognised (Trans., 1885, 47, 242) that ethyl benzoylacetate itself is readily hydrolysed by concentrated sulphuric acid in the cold, with formation of benzoylactic acid, but this simple method did not apply to the mono- or di-substitution derivatives, which, under these conditions, either remained unchanged or were hydrolysed with elimination of carbon dioxide and formation of substitution derivatives of acetophenone, and these results we can confirm. Experiments on the action of alcoholic potassium hydroxide under different conditions on the mono- or di-substitution derivatives of ethyl benzoylacetate yielded unsatisfactory results, since the products, which we were able to isolate, were usually only benzoic acid and substituted acetophenones.

On the other hand, dilute potassium hydroxide (3 per cent.) gradually dissolves the mono-substitution derivatives of ethyl benzoylacetate, and, after remaining for two days and then acidifying and extracting with ether, the mono-substituted benzoylactic acid is obtained. We have thus prepared α -benzoylpropionic acid (m. p. 82—83°) and α -benzoylbutyric acid (m. p. 85—87°) in a pure state.

The disubstitution derivatives of ethyl benzoylacetate are insoluble in dilute alkalis, and we have been unable to find any conditions which yield the corresponding acids. In all experiments where hydrolysis took place, it was accompanied by the simultaneous elimination of carbon dioxide and formation of substituted acetophenones and benzoic acid. The melting points of benzoyl-, ethyl-, allyl-, and diethyl-acetic acids (α -benzoyl-butyric, -allylacetic, and - α -ethylbutyric acids) given in the earlier paper (Trans., 1884, 45, 180) as 115°, 122°, and 128—130°* respectively are incorrect. There can be no doubt that the acids were produced in the way described, but, unfortunately, the final melting points were not taken until several months after the analyses had been made, and while the results were being written for publication; during this time decomposition had evidently taken place, in each case with formation of benzoic acid.

* This should have been 118—120°.

EXPERIMENTAL.

Ethyl α -Benzoylpropionate, $C_6H_5 \cdot CO \cdot CHMe \cdot CO_2Et$, *Ethyl α -Benzoyl-isobutyrate*, $C_6H_5 \cdot CO \cdot CMe_2 \cdot CO_2Et$, and *Ethyl α -Benzoyl- β -phenyl-isobutyrate*, $C_6H_5 \cdot CH_2 \cdot CMeBz \cdot CO_2Et$.

Ethyl α -benzoylpropionate has already been described by Perkin and Calman (ethyl benzoylmethylacetate: *Trans.*, 1886, **49**, 156) as a colourless oil boiling at $235^\circ/300$ mm. We have prepared considerable quantities of this ester by mixing ethyl benzoylacetate (30 grams) with sodium ethoxide (containing 3.6 grams of sodium), adding methyl iodide, and heating on the water-bath for one hour. It distilled at $162\text{--}163^\circ/18$ mm., and yielded correct results on analysis:

0.1165 gave 0.2976 CO_2 and 0.0731 H_2O . C=69.6; H=6.9.

$C_{12}H_{14}O_3$ requires C=69.9; H=6.8 per cent.

α -Benzoylpropionic acid, $C_5H_5 \cdot CO \cdot CHMe \cdot CO_2H$.—Perkin and Calman (*loc. cit.*, p. 157) attempted to prepare this acid by using the conditions which so readily convert ethyl benzoylacetate into benzoylacetic acid, namely, hydrolysis with concentrated sulphuric acid at the ordinary temperature, but without success. We have also made a number of experiments in the same direction, and find that, under these conditions, the ester either remains unchanged or is decomposed, with formation of a neutral oil, which is doubtless propiophenone. Ultimately, we were successful in preparing considerable quantities of the acid in the following way. Ethyl α -benzoylpropionate (1 mol.) was mixed with a 3 per cent. aqueous solution of potassium hydroxide (2 mols.), and well shaken from time to time, and until almost the whole quantity had dissolved. After about two days, the remaining neutral oil was extracted with ether, the aqueous solution mixed with ice, and acidified, when an oily acid separated, which soon crystallised. This was collected, left in contact with porous porcelain until quite dry, and then crystallised from a mixture of benzene and light petroleum:

0.1850 gave 0.4565 CO_2 and 0.0899 H_2O . C=67.3; H=5.4.

$C_{10}H_{10}O_3$ requires C=67.4; H=5.6 per cent.

When titrated with $N/10$ -barium hydroxide, 0.3885 neutralised 0.1990 $Ba(OH)_2$, whereas this amount of a monobasic acid, $C_{10}H_{10}O_3$, should neutralise 0.1881 $Ba(OH)_2$.

α -Benzoylpropionic acid separates from a mixture of benzene and light petroleum in colourless, glistening crystals, melts at $82\text{--}83^\circ$ with evolution of gas, and gives only a brown coloration when ferric chloride is added to its alcoholic solution. The ester from which the acid had been prepared gave a faint violet

coloration with ferric chloride, which was doubtless due to the presence of traces of ethyl benzoylacetate, and the statement of Perkin and Calman (*loc. cit.*) that ethyl benzoylmethylacetate (α -benzoylpropionate) gives no coloration with ferric chloride is probably correct. If this be so, there is a striking difference in this particular between the mono-substitution derivatives of ethyl benzoylacetate and those of ethyl acetoacetate, since the latter give intense violet colorations with ferric chloride.

Ethyl α -benzoylisobutyrate, $C_6H_5 \cdot CO \cdot CMe_2 \cdot CO_2Et$.—This di-substitution derivative may be obtained in a yield of 60 to 70 per cent. of that theoretically possible by the following method of preparation.

Ethyl α -benzoylpropionate (15 grams) is added to finely divided sodium* (1.8 grams) suspended in toluene, and, after remaining for three hours, the toluene solution is decanted from traces of undissolved sodium, mixed with methyl iodide (11 grams), and heated to boiling for three hours. The product is mixed with ether, washed with water and dilute hydrochloric acid, dried, and, after removing the toluene and ether by evaporation, an oil is obtained which distils at 153—156°/19 mm., and gives no coloration when ferric chloride is added to its alcoholic solution:

0.1441 gave 0.3748 CO_2 and 0.0967 H_2O . C=70.9; H=7.4.

$C_{13}H_{16}O_3$ requires C=70.9; H=7.3 per cent.

There can be no doubt that this oil is practically pure ethyl α -benzoylisobutyrate, but subsequent experience (p. 2049) shows that it would be desirable, on future occasions, to treat this oil with aqueous potassium hydroxide, in order to remove traces of ethyl α -benzoylpropionate which it may possibly contain. Many experiments were made with the object of obtaining α -benzoylisobutyric acid by the hydrolysis of this ester, but they were all unsuccessful. When left in contact with concentrated sulphuric acid for two days, it remained mostly unchanged, but was partly decomposed, with the formation of neutral oils. The action both of aqueous and alcoholic potassium hydroxide led to the formation of much benzoic acid.

Ethyl α -benzoyl- β -phenylisobutyrate, $C_6H_5 \cdot CH_2 \cdot CMeBz \cdot CO_2Et$.—This substance is readily obtained when ethyl α -benzoylpropionate (12.3 grams) is added to finely-divided sodium (1.7 grams) suspended in toluene, and, after remaining for three hours, the toluene solution is decanted, mixed with benzyl chloride (7.6 grams), and heated to boiling for three hours. The product, isolated in the usual manner, distilled at 223—228°/19 mm., and gave no coloration on the addition of ferric chloride to its alcoholic solution. Analysis

* Prepared by melting sodium under toluene and shaking vigorously.

showed that this substance was pure *ethyl α -benzoyl- β -phenyl-isobutyrate*:

0.1228 gave 0.3450 CO_2 and 0.0781 H_2O . C = 76.6; H = 7.0.

$\text{C}_{19}\text{H}_{20}\text{O}_3$ requires C = 77.0; H = 6.7 per cent.

In the case of this disubstitution derivative, also, many attempts were made to obtain the free acid by hydrolysis either with alkalis or acids, but without success.

Ethyl α -Benzoylbutyrate, $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CHEt}\cdot\text{CO}_2\text{Et}$, *Ethyl α -Benzoyl- α -ethylbutyrate*, $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CEt}_2\cdot\text{CO}_2\text{Et}$, *Ethyl α -Benzoyl- α -methylbutyrate*, $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CMeEt}\cdot\text{CO}_2\text{Et}$, and *Ethyl α -Benzoyl- β -phenyl- α -ethylpropionate*, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CEtBz}\cdot\text{CO}_2\text{Et}$.

The ethyl α -benzoylbutyrate employed in the following experiments was prepared exactly as described by Perkin (Trans., 1884, 45, 179; 1885, 47, 241), namely, by adding ethyl benzoylacetate (5 grams), and then ethyl iodide (10 grams), to a solution of 0.6 gram of sodium in 15 c.c. of absolute alcohol. After heating on the water-bath for about an hour and a-half, the product was isolated in the usual manner, and purified by fractionation under diminished pressure.

It distilled at 168—171°/19 mm., and gave a faint violet coloration when ferric chloride was added to its alcoholic solution:

0.1307 gave 0.3396 CO_2 and 0.0860 H_2O . C = 70.8; H = 7.3.

$\text{C}_{13}\text{H}_{16}\text{O}_3$ requires C = 70.9; H = 7.3 per cent.

Perkin (*loc. cit.*) gives 210—211°/90 mm. as the boiling point of this ester.

α -Benzoylbutyric acid, $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CHEt}\cdot\text{CO}_2\text{H}$.—Although ethyl benzoylacetate is so readily converted into benzoylacetic acid by concentrated sulphuric acid in the cold, ethyl α -benzoylbutyrate is only very slowly attacked under the same conditions, and much ester remains undecomposed even after solution in a large excess of sulphuric acid for fourteen days. When the ester is allowed to remain for two days with methyl-alcoholic potassium hydroxide (15 per cent.) at the ordinary temperature, a considerable quantity of potassium carbonate separates, and a neutral oil is formed, which distils principally at about 210—220°, and evidently consists mainly of phenyl propyl ketone. The alkaline solution yields, on acidifying, a copious precipitate of benzoic acid. Similar results were obtained with dilute methyl-alcoholic potassium hydroxide (3 per cent.), but ultimately it was found that α -benzoylbutyric acid may be obtained in a pure condition by employing aqueous alkali under the following conditions. Ethyl α -benzoylbutyrate (1 mol.) is shaken mechanically with 3 per cent. aqueous potassium

hydroxide (2 mols.) for two days, and the neutral oil removed by extraction with ether. The alkaline solution is mixed with ice, acidified, extraction with pure ether, the ethereal solution dried and evaporated at as low a temperature as possible, when a colourless oil is obtained which soon crystallises. After remaining in contact with porous porcelain until quite free from oily impurity, the acid was cautiously crystallised from a mixture of benzene and light petroleum:

0.1595 gave 0.4002 CO_2 and 0.0952 H_2O . C = 68.4; H = 6.6.

0.1620 ,, 0.4107 CO_2 ,, 0.0916 H_2O . C = 69.1; H = 6.2.

$\text{C}_{11}\text{H}_{12}\text{O}_3$ requires C = 68.8; H = 6.2 per cent.

On titration with *N*/10-barium hydroxide, 0.5533 neutralised 0.2413 $\text{Ba}(\text{OH})_2$, whereas this amount of a monobasic acid, $\text{C}_{11}\text{H}_{12}\text{O}_3$, should neutralise 0.2484 gram.

α -Benzoylbutyric acid separates from a mixture of benzene and light petroleum in colourless, glistening plates, and melts at 85–87° with evolution of gas.

It appears to be more unstable than the corresponding methyl acid (α -benzoylpropionic acid), since on keeping, even in a stoppered tube, it gradually becomes sticky, whereas the latter remains crisp under the same conditions.

Ethyl α -benzoyl- α -ethylbutyrate, $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CET}_2\cdot\text{CO}_2\text{Et}$.—In the earlier research (Perkin, *Trans.*, 1884, **45**, 182), an attempt was made to introduce a second ethyl group into ethyl α -benzoylbutyrate by treating it with sodium ethoxide and ethyl iodide in the usual manner, and, although the product was not purified by distillation,* its examination was thought to indicate that it consisted in the main of ethyl α -benzoyl- α -ethylbutyrate. We now find that it is very difficult to introduce a second ethyl group into ethyl α -benzoylbutyrate, and the yield of ethyl α -benzoyl- α -ethylbutyrate obtained, even under the best conditions, is only small.

In the first experiments, ethyl α -benzoylbutyrate was digested, in alcoholic solution, with the theoretical amount of sodium ethoxide and excess of ethyl iodide. The product, isolated in the usual manner, was found to distil almost entirely below 160°/20 mm., and the distillate evidently consisted mainly of ethyl derivatives of acetophenone, hydrolysis having taken place under the conditions employed. Since it was possible that the large amount of sodium ethoxide present at the beginning might have produced the hydrolysis, the experiment was repeated, with this

* At the time this research was carried out, the method of fractionating under diminished pressures, now so common, had not been developed.

difference, that the alcoholic sodium ethoxide was added drop by drop to the mixture of ethyl α -benzoylbutyrate and ethyl iodide, but, in this case also, the product consisted principally of neutral oils, together with some ethyl benzoate. Negative results were also obtained when ethyl α -benzoylbutyrate was treated, in dry ethereal solution, with sodium, and then with ethyl iodide. Ultimately it was found that ethyl α -benzoyl- α -ethylbutyrate may be prepared, although in small yield, by the following process. Ethyl α -benzoylbutyrate (22 grams) is added to finely-divided sodium (2.3 grams) suspended in toluene,* and left until almost the whole of the sodium has dissolved; the red toluene solution is then decanted from any unchanged sodium, and heated on the sand-bath with excess of ethyl iodide. The product, isolated as usual, yielded a considerable fraction, distilling at 176—179°/20 mm., which, on analysis, gave numbers intermediate between those required for ethyl α -benzoylbutyrate and ethyl α -benzoyl- α -ethylbutyrate. In order to remove the former, the mixture was shaken mechanically with a considerable excess of 3 per cent. aqueous potassium hydroxide for two days, and the unhydrolysed oil extracted with ether. It now distilled at 179—183°/20 mm., gave no coloration with ferric chloride, and evidently consisted of pure ethyl α -benzoyl- α -ethylbutyrate:

0.1311 gave 0.3488 CO₂ and 0.0921 H₂O. C = 72.5; H = 7.8.

C₁₅H₂₀O₃ requires C = 72.5; H = 8.0 per cent.

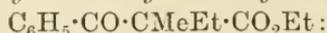
The yield obtained was approximately 20 per cent. of that theoretically possible. In order to determine the reason for the small yield of ethyl α -benzoyl- α -ethylbutyrate, even under the most favourable circumstances, an experiment was made with the object of ascertaining whether this might be due to the sodium derivative of ethyl α -benzoylbutyrate undergoing decomposition before it reacted with the ethyl iodide.

The sodium derivative was prepared in toluene solution, and digested on the sand-bath, care being taken to exclude moisture, but, even after boiling for five hours, no appreciable decomposition could be detected, and almost all the ester was recovered unchanged. That the smallness of the yield of ethyl α -benzoyl- α -ethylbutyrate obtained in the experiments described above is, in some way, partly due to the comparatively slow action of the ethyl iodide is clearly indicated in the following experiments.

I. The sodium derivative of ethyl α -benzoylbutyrate was prepared in toluene solution, digested with excess of methyl iodide in the usual manner, and the product, after distillation, shaken mechanically with an excess of 3 per cent. aqueous potassium

* See footnote, p. 2046.

hydroxide for two days. The unhydrolysed ester distilled at 163—165°/18 mm., gave no coloration with ferric chloride, and consisted of pure *ethyl α-benzoyl-α-methylbutyrate*,



0·1120 gave 0·2932 CO₂ and 0·0787 H₂O. C=71·4; H=7·8.

C₁₄H₁₈O₃ requires C=71·8; H=7·7 per cent.

The yield of ester obtained in this experiment was roughly 60 per cent. of that theoretically possible, and, when the alkaline extract was acidified, there was only a slight turbidity, and no *α*-benzoylbutyric acid separated on standing.

II. The sodium derivative of ethyl *α*-benzoylpropionate was digested, under the same conditions as in (I), with excess of ethyl iodide, and the product, after treatment with potassium hydroxide, yielded an oil which distilled at 165—167°/20 mm., and consisted of ethyl *α*-benzoyl-*α*-methylbutyrate:

0·1528 gave 0·4033 CO₂ and 0·1066 H₂O. C=71·9; H=7·7.

C₁₄H₁₈O₃ requires C=71·8; H=7·7 per cent.

In this experiment, the yield obtained was considerably less than in (I), and, when the alkaline extract was acidified, a precipitate of *α*-benzoylpropionic acid separated after some time, showing that the decomposition of the sodium derivative of the ethyl *α*-benzoylpropionate by the ethyl iodide had not been complete.

III. In order to obtain further evidence that the rapidity of action of the halogen derivative employed for substitution has something to do with the yield of disubstitution product, the action of benzyl chloride on the sodium derivative of ethyl *α*-benzoylbutyrate was investigated. Ethyl *α*-benzoylbutyrate (15 grams) was converted into the sodium derivative by the action of sodium (1·6 grams) on its toluene solution, as in the previous cases, pure benzyl chloride (12 grams) was then added, and the whole boiled for one hour.

The product, isolated in the usual manner, distilled almost completely at 225—229°/17 mm., gave no coloration with ferric chloride, and consisted of pure *ethyl α-benzoyl-β-phenyl-α-ethylpropionate*, C₆H₅·CH₂·CEtBz·CO₂Et:

0·1296 gave 0·3683 CO₂ and 0·0842 H₂O. C=77·5; H=7·2.

C₂₀H₂₂O₃ requires C=77·4; H=7·1 per cent.

The yield of this disubstitution derivative was more than 75 per cent. of that theoretically possible.

These experiments do not sufficiently account for the smallness of the yield obtained when the sodium derivative of ethyl *α*-benzoylbutyrate is digested with ethyl iodide, and it is just possible that this may be due to the decomposition of the ethyl iodide into

ethylene and hydrogen iodide during the prolonged boiling in toluene solution. Experiments will be instituted in order to determine whether such decomposition actually takes place under these conditions, because, if this were so, the liberated hydrogen iodide might well decompose some of the ester, and thus account for the small yield of the diethyl substitution derivative.

The authors wish to state that much of the expense of this investigation was met by a grant from the Research Fund of the Chemical Society.

THE SCHUNCK LABORATORY,
THE UNIVERSITY,
MANCHESTER.

CCXXIV.—*Studies in the Camphane Series. Part XXVII. Camphorylphenyltriazen (Camphordiazoaminobenzene) and its Bearing on the Constitution of Diazoamino-compounds.*

By MARTIN ONSLOW FORSTER and CHARLES SAMUEL GARLAND.

SINCE the discovery of the first diazoamino-compound by Griess, the problems connected with the constitution of triazen derivatives have maintained their interest for chemists to the present day; whilst, however, the investigation of aromatic diazoamines has been continuous, the progress of the branch dealing with aliphatic-aromatic triazens has been intermittent. That such derivatives are obtainable from diazonium salts and aliphatic secondary amines was shown by Baeyer and Jaeger (*Ber.*, 1875, **8**, 148 and 893), and by Wallach (*Annalen*, 1886, **235**, 233); it was found also that bisdiazoamino-derivatives arise from aliphatic primary amines (H. Goldschmidt and Holm, *Ber.*, 1888, **21**, 1016; H. Goldschmidt and Badl, *Ber.*, 1889, **22**, 933),



a normal diazoamine being produced only from benzylamine (Goldschmidt and Holm, *loc. cit.*). Here the subject remained apparently untouched until 1903, when Dimroth discovered that aliphatic-aromatic triazens may be synthesised by an application of the Grignard reaction to organic azoimides (*Ber.*, 1903, **36**, 909), and this observation has been so fruitful in the hands of its author that a new series of diazoamino-compounds containing

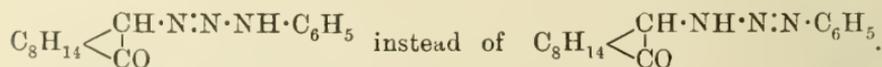
alkyl groups has been brought to light, of which the most remarkable member is diazoaminomethane, or dimethyltriazene, produced by the action of magnesium methyl iodide on methylazoimide (Dimroth, *Ber.*, 1906, **39**, 3905; compare also Dimroth, *Ber.*, 1905, **38**, 670; Dimroth, Eble, and Gruhl, *Ber.*, 1907, **40**, 2390).

The principal point of interest in connexion with aliphatic-aromatic triazenes, as with those of purely benzenoid origin, lies in their dynamic isomerism, and it appeared to us probable that an investigation of the diazoamines theoretically obtainable from aminocamphor and methylaminocamphor would help to free this part of the subject from the obscurity which still prevails. Keeping in mind the readiness with which diazo- ψ -semicarbazines are produced from camphoryl- ψ -semicarbazide (*Trans.*, 1906, **89**, 222), we have subjected aminocamphor and its methyl derivative to the action of diazonium salts, and find that in absence of mineral acid coupling proceeds smoothly but slowly; by observing certain precautions specified below, the products may be isolated and crystallised. According to this method of formation, the simplest members of the two classes would be represented respectively by the formulæ:



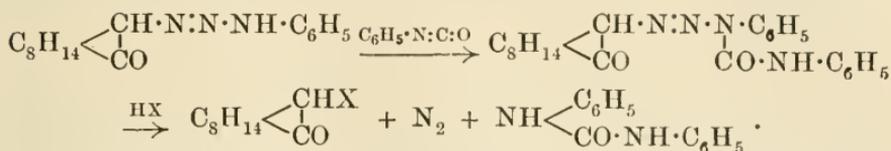
and as regards the derivatives of methylaminocamphor there is no doubt that the latter expression is faithful to the facts; camphorylphenylmethyltriazene and its substitution products are sufficiently stable towards mineral acids to form definite, crystalline salts which, when warmed with dilute acids, are resolved into methylaminocamphor and the corresponding diazonium salt.

Camphorylphenyltriazene, on the other hand, is highly sensitive towards mineral acids, and even acetic or picric acid is able to liberate nitrogen from it; no member of the series which includes its derivatives, with one exception to be mentioned later, gives the slightest indication of a diazonium chloride when treated with hydrochloric acid. Taken alone, therefore, the behaviour of camphorylphenyltriazene towards acids would suggest the character of camphordiazoaminobenzene rather than that of benzenediazoaminocamphor:

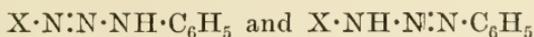


This indication is confirmed by the behaviour of the substance towards phenylcarbimide, which transforms it into camphordiazo-diphenylcarbamide, the structure of which is established by its

resolution into diphenylcarbamide, nitrogen, and a camphor residue, without a trace of diazonium salt:



This is the first time that agreement between the course of the attack by phenylcarbimide and that of the acid resolution has been observed in connexion with aliphatic-aromatic diazoamino-compounds. Dimroth, in a communication already quoted (*Ber.*, 1905, **38**, 670), has made it plain that phenylmethyltriazen, phenylethyltriazen, and phenylbenzyltriazen are resolved by hydrogen chloride into aniline, nitrogen, and the corresponding alkyl chloride, whilst phenylcarbimide converts them into carbamide derivatives, from which, in each case, benzenediazonium salt is removed by acids, whence it follows that Dimroth's triazens would appear to behave towards acids and phenylcarbimide according to the formulæ:



respectively, where X represents the alkyl or substituted alkyl group.

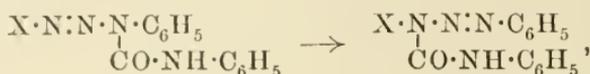
For a reason which will now appear, we believe that this inconsistency in the attitude of Dimroth's triazens towards hydrogen chloride, on the one hand, and phenylcarbimide, on the other, is illusory, and is due to the non-appearance of an intermediate carbamide arising from $\text{X} \cdot \text{N} \cdot \text{N} \cdot \text{NH} \cdot \text{C}_6\text{H}_5$. We base this view on the observation that the camphordiazodiphenylcarbamide obtained from camphorylphenyltriazen and phenylcarbimide is transformed quantitatively and with great facility into an isomeric substance,



which, in distinction from its generator, yields benzenediazonium salt on resolution by acids. Although this rearrangement involves the migration of the phenylcarbamic radicle, $\text{C}_6\text{H}_5 \cdot \text{NH} \cdot \text{CO}$, it seems to us the only possible interpretation of the facts, and if accepted must lead, in our opinion, to the recognition of Dimroth's triazens and of camphorylphenyltriazen itself as diazoamino-compounds of the type $\text{X} \cdot \text{N} \cdot \text{N} \cdot \text{NH} \cdot \text{C}_6\text{H}_5$, where X represents the alkyl and camphoryl groups. In other words, the conflicting evidence brought to light by Dimroth is probably due, not to a tautomeric change induced by hydrogen chloride in the direction:

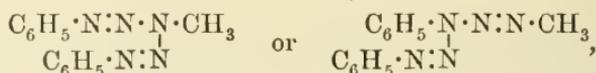


followed by resolution of the triazen into alkyl chloride, nitrogen, and aniline, but rather to a molecular transformation of the diazo-carbamide:

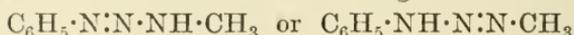


proceeding so rapidly that only in the case of the heavily-weighted camphor derivative has it as yet been possible to arrest the change at its initial stage.* Even the diazo-carbamide from camphoryl-phenyltriazen, although stable in the solid state, changes very rapidly when dissolved, and, being optically active, affords an opportunity to follow the alteration in the polarimeter.

The foregoing conclusion as to the constitution of the aliphatic-aromatic triazens being opposed to that of Dimroth and of H. Goldschmidt (*loc. cit.*, and *Ber.*, 1905, **38**, 1096), it is necessary to refer to those experiments of the former investigator with Eble and Gruhl (*Ber.*, 1907, **40**, 2390) which led him to the opinion indicated. These consisted in preparing bisdiaz-amino-compounds from the aliphatic-aromatic triazens by the action of diazonium salts, and in examining the products of resolving them with alcoholic acid. The quoted authors premise that the bisdiaz-amino-compound from phenylmethyltriazen and benzenediazonium chloride should be:



according to the constitution of the original triazen being:

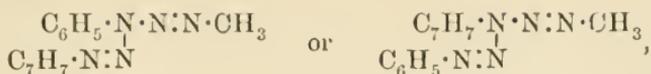


respectively, but although they found that the bisdiaz-amino-compound, instead of yielding methylamine and two molecules of benzenediazonium salt, breaks up into one molecule of elemental nitrogen and one molecule of diazonium salt, they nevertheless reject the unsymmetrical formula, and prefer the symmetrical one. Their reason for doing so is the observation that the product of coupling toluenediazonium chloride with phenylmethyltriazen is identical with that obtained from tolylmethyltriazen and benzenediazonium chloride, whence they conclude that it has the constitution:



* It is proposed, however, to re-examine the behaviour of some among the better known diazo-amino-compounds towards phenylcarbimide from the new standpoint in the hope of establishing other cases in which the initial diazo-carbamide may be isolated. Our experiments suggest that by working in darkness and by selecting appropriate solvents, isomerism of the type which occurs in the camphor series may be revealed elsewhere.—M. O. F.

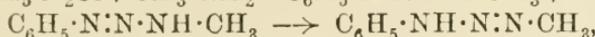
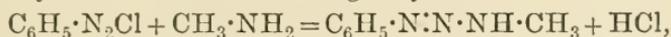
rather than:



and explain the production of nitrogen (1 mol.) and diazonium salt (1 mol.) by assuming the regeneration of the triazen.

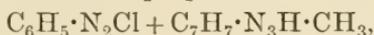
For the following reasons the evidence from the bisdiazooamino-compounds is not, in our opinion, of a character to overthrow the formula, $\text{X} \cdot \text{N} \cdot \text{N} \cdot \text{NH} \cdot \text{C}_6\text{H}_5$, for the aliphatic-aromatic triazens.

1. Dimroth and his colleagues have shown that the bisdiazooamino-derivative from phenylmethyltriazen and benzenediazonium salt is identical with the product from methylamine and two molecules of benzenediazonium salt, and that it is resolved by acids into one molecule of diazonium salt and one molecule of nitrogen along with aniline and methyl chloride. At first they were disposed to interpret this as proving that the bisdiazooamino-compound arises from methylamine in the following way:



$\text{C}_6\text{H}_5 \cdot \text{N}_2\text{Cl} + \text{C}_6\text{H}_5 \cdot \text{NH} \cdot \text{N} \cdot \text{N} \cdot \text{CH}_3 = \text{C}_6\text{H}_5 \cdot \text{N}(\text{N}_2 \cdot \text{C}_6\text{H}_5) \cdot \text{N} \cdot \text{N} \cdot \text{CH}_3 + \text{HCl}$, and this appears to us a more reasonable explanation than to assume that the symmetrical bisdiazooamino-compound would yield only one molecule of diazonium salt.

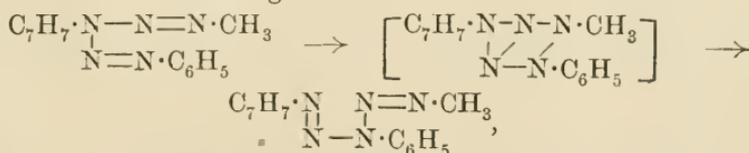
2. The unsymmetrical structure, $\text{C}_6\text{H}_5 \cdot \text{N}(\text{N}_2 \cdot \text{C}_7\text{H}_7) \cdot \text{N} \cdot \text{N} \cdot \text{CH}_3$, for the bisdiazooamino-derivative prepared from



and from



and rejected by the quoted authors as involving migration of the $\text{R} \cdot \text{N}_2$ -complex, in spite of its apparent sequence from the production of toluenediazonium chloride, aniline, nitrogen, and methyl chloride by the action of hydrochloric acid, is not so improbable as to be dismissed in face of this strong evidence supporting it, now that Dimroth's own most interesting observations in the tribenzoylmethane series (Dimroth and Hartmann, *Ber.*, 1908, **41**, 4012) have shown that a benzene-*O*-azo-compound may change into the isomeric benzene-*C*-azo-derivative on fusion. Moreover, the transformation of diazoaminobenzene into aminoazobenzene probably depends on a similar migration, which, if still repugnant, may be evaded or explained in the following manner:



representing the existence of an intermediate condition of the molecule, not materialised experimentally, where some play of force occurs between the two pairs of doubly linked nitrogen atoms.

3. It is hardly consistent to base conclusions regarding the constitution of the bisdiazamino-compounds upon the products of resolution by acids, when the products of resolving the triazens themselves, pointing as they emphatically do to the expression $X \cdot N : N \cdot NH \cdot C_6H_5$, are ignored.

A general survey of the evidence, then, appears to us firmly to establish the formula $X \cdot N : N \cdot NH \cdot C_6H_5$ for the aliphatic-aromatic triazens, and it is to be supposed that in the process of formation by coupling the diazonium salt and the primary amine, sufficient attraction for the hydrogen atom is exerted by the more negative phenyl group to effect the transformation:



It is noteworthy that more than twenty years ago H. Goldschmidt and Molinari (*Ber.*, 1888, **21**, 2578) laid down this principle for aromatic diazomino-compounds containing different radicles, while rejecting it for benzylphenyltriazene, because of the structure of the diazocarbamide obtained by the action of phenylcarbimide. We are inclined to the view that a closer examination of the aromatic triazens, $X \cdot N_3H \cdot Y$, will show them also to be embraced by the generalisation in question, as claimed by Goldschmidt and Molinari, and, although aware that much experimental work has been recorded in opposition, we attach considerable importance to the following considerations in support of it.

1. The competition between two aryl groups for the hydrogen atom of the triazene chain being so much more evenly balanced than that occurring between an aromatic and an aliphatic residue, it is reasonable to suppose that environment is the dominant factor in phenomena which fail to distinguish between $X \cdot N : N \cdot NH \cdot Y$ and $X \cdot NH \cdot N : N \cdot Y$.

2. The numerous cases of resolution by acids upon which current views regarding the constitution of aromatic diazomino-compounds are based would appear, most frequently, to have been studied at temperatures ranging from that of the laboratory to 100°, instead of at zero, or below. It is highly significant that phenyl- α -naphthyltriazene, whether prepared from α -naphthylazoimide and magnesium phenyl bromide, or from magnesium α -naphthyl bromide and phenylazoimide, should yield aniline and α -naphthalenediazonium chloride without naphthylamine when resolved by alcoholic hydrochloric acid in a freezing mixture (Dimroth, Eble, and Gruhl, *loc. cit.*, 2401).

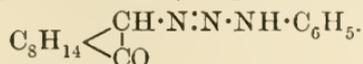
3. There does not appear to have been recorded a case in which

two isomeric diazocarbamides have arisen by direct action of phenylcarbimide on a diaryltriazen.

In conclusion, it may perhaps be worth while to point out that the isomeric transformation of the diazocarbamide obtained by the direct action of phenylcarbimide on camphorylphenyltriazen constitutes fresh evidence as to the untrustworthy character of this agent in problems concerning the elucidation of structure (compare Michael, *Ber.*, 1905, **38**, 22).

EXPERIMENTAL.

Camphorylphenyltriazen (Camphordiazoaminobenzene),



An alkaline solution of aminocamphor was prepared by dissolving 30 grams of the carbonate in dilute acetic acid, and adding 20 per cent. sodium carbonate; 10 grams of aniline were diazotised, and the liquid having been rendered alkaline with sodium carbonate, the ice-cold solutions were mixed. The appearance did not change at first, but a pale brown, flocculent precipitate followed the addition of 20 per cent. sodium carbonate, 250 c.c. of which were used; the solid product was augmented by dissolving 100 grams of crystallised sodium acetate in the liquid, which was filtered after half an hour.

Throughout the coupling process the materials were protected from light, towards which the triazens are sensitive, and it was found more conducive to rapid filtration not to use the pump; the washed product was roughly dried on porous earthenware and dissolved in a small quantity of chloroform, from which the suspended water was removed by sodium sulphate, and on adding about five times its bulk of petroleum (b. p. 80—100°) to the dark brown, filtered solution, the triazen separated during spontaneous evaporation. Recrystallisation from a mixture of chloroform and petroleum gave well-defined, pale brown, centimetre-long prisms, the substance being obtained almost colourless by dissolution in boiling petroleum (60—80°), which deposits lustrous needles on cooling:

0.1879 gave 25.6 c.c. N_2 at 18° and 760 mm. $\text{N} = 15.74$.

$\text{C}_{16}\text{H}_{21}\text{ON}_3$ requires $\text{N} = 15.50$ per cent.

Camphorylphenyltriazen decomposes at about 150°, the temperature varying according to the rate at which it is raised. It is slightly soluble in boiling water, which does not decompose it, but dissolves freely in cold methyl and ethyl alcohols, ethyl acetate, acetone, chloroform, ether, or benzene, more sparingly in hot

petroleum; a solution containing 0.3907 gram, made up to 25 c.c. with chloroform, gave $\alpha_D^{20} 0^\circ 35'$ in the 2-dcm. tube, whence $[\alpha]_D^{18} 18.6^\circ$.

When covered with cold glacial acetic acid, the substance dissolved, and slow liberation of gas began soon afterwards; with an alcoholic solution of picric acid, gas was evolved very slowly, the pale yellow solution rapidly becoming orange. On passing dry hydrogen chloride into an ethereal solution of camphorylphenyltriazene, bubbles of gas quickly appeared, along with a white precipitate, which dissolved on adding water; the aqueous solution gave a negative result when poured into alkaline β -naphthol, containing only aniline hydrochloride, which was identified by conversion into acetanilide. Moreover, when rubbed with ice-cold hydrochloric acid, the crystals became viscous and intumescenced, but the acid liquor did not develop a coloration with alkaline β -naphthol, and the addition of concentrated hydrochloric acid to a freshly prepared solution in glacial acetic acid was equally fruitless in this respect, although giving rise to vigorous effervescence. Further evidence as to the position of the mobile hydrogen atom was adduced by the indifference of an alcoholic solution towards *m*-phenylenediamine hydrochloride, which immediately reddens diazoaminobenzene, and also by the observation that a solution of camphorylphenyltriazene in phenol may be heated gradually until the decomposing point is reached without change of colour; finally, a solution of the substance in pyridine containing β -naphthol was heated to the boiling point without any indication of benzeneazo- β -naphthol being produced.

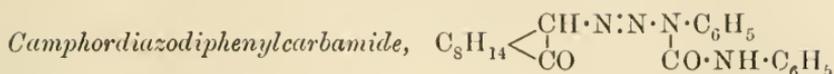
The *silver* derivative arose from an attempt to methylate the triazene by leaving a solution in chloroform with silver oxide and methyl iodide in the dark room during three days; the filtered liquid was diluted with petroleum and allowed to evaporate spontaneously, when a transparent, pale brown varnish remained. Cold acetone converted this into a crystalline paste, and, after recrystallisation from boiling acetone, greenish-yellow needles were obtained:

0.1416 gave 0.0540 AgCl. Ag = 28.72.

$C_{16}H_{20}ON_3Ag$ requires Ag = 28.57 per cent.

The substance became dark brown at about 150° , afterwards blackening, and undergoing complete decomposition at 180° .

We failed to transform the silver derivative into camphorylphenylmethyltriazene by the action of methyl iodide, and a similar want of success in connexion with phenylmethyltriazene is recorded by Dimroth (*Ber.*, 1905, **38**, 679); action appears to occur, but not in the direction anticipated.



Nine grams of freshly prepared, recrystallised camphorylphenyl-triazen, dissolved in 100 c.c. of benzene (dried with sodium), were left with 4 grams of phenylcarbimide in a stoppered vessel protected from light; after forty-eight hours the odour of isocyanate was not longer perceptible, and 11 grams of crystals had separated, the remainder of the product (1 gram) being precipitated by petroleum. Recrystallisation from hot petroleum (b. p. 60—80°) gave lustrous, colourless needles, melting with complete decomposition at 147°:

0.1980 gave 25.4 c.c. N_2 at 24° and 758 mm. $N = 14.35$.

$C_{23}H_{26}O_2N_4$ requires $N = 14.36$ per cent.

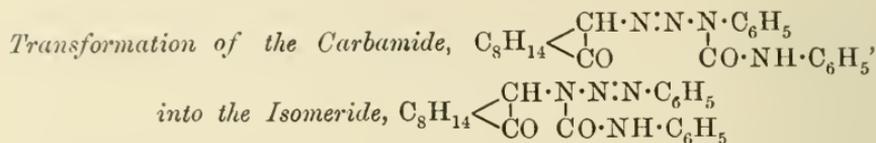
The substance is freely soluble in cold chloroform, less readily in methyl and ethyl alcohols, benzene, ethyl acetate, or acetone, whilst boiling petroleum dissolves it very sparingly, nearly 1000 c.c. being required by 1 gram. Owing to the readiness with which it is transformed into the isomeride by acetone, pyridine, and the alcohols, the safest means of recrystallising it is extraction with hot petroleum, or precipitation from the benzene solution by cold petroleum. A solution containing 0.1002 gram, made up to 20 c.c. with dry pyridine, gave $\alpha_D 1^{\circ}33'$ in the 2-dcm. tube when examined immediately, rising to $2^{\circ}7'$ in twenty-four hours; this corresponds with $[\alpha]_D 154.7^{\circ}$ for the substance itself, and indicates almost complete transformation into the isomeric carbamide within the period stated, $[\alpha]_D 211.4^{\circ}$ instead of 220.6° . The carbamide becomes deep yellow when covered with cold concentrated hydrochloric acid, but gas is not liberated until the temperature is raised, and the diluted liquid does not develop colour with alkaline β -naphthol; furthermore, coupling does not occur in either acetic acid or pyridine.

Resolution by Glacial Acetic Acid.—When the substance is covered with cold glacial acetic acid, there is no change in appearance, and gas is not set free, but, on warming the liquid, dissolution occurs, brisk effervescence takes place, and crystals of diphenylcarbamide separate from the liquid; attempts to identify the form of the camphor residue have failed, the neutralised filtrate from diphenylcarbamide yielding on steam distillation a pale yellow oil having a pleasant odour. On carrying out the above experiment in a flask communicating with a nitrometer, and sweeping out air by means of carbon dioxide, the amount of gas could be measured:

0.2383 gave 15.6 c.c. N_2 at 23° and 764 mm. $N = 7.4$.

$C_{23}H_{26}O_2N_4$ requires $\frac{1}{2}N = 7.2$ per cent.

The diphenylcarbamide melted at 235° after recrystallisation, and gave $N = 13.1$ per cent. ($C_{13}H_{12}ON_2$ requires $N = 13.2$ per cent.).



Although the carbamide (m. p. 147°) which arises by direct action of phenylcarbimide on camphorylphenyltriazen readily loses nitrogen when warmed with glacial acetic acid, the element is not liberated when a solution in pyridine is raised to the boiling point. The change which takes place is the rearrangement indicated in the headline, and in order to accomplish this it is not even necessary to heat the solution, exposure to light during one to two days being sufficient. On diluting the pyridine largely with water, minute, felted needles are precipitated, having the same weight as the original material; recrystallisation from hot absolute alcohol, followed by glacial acetic acid, raises the melting point to 209° , when complete decomposition takes place:

0.2134 gave 27.3 c.c. N_2 at 24° and 763 mm. $N = 14.40$.

$C_{23}H_{26}O_2N_4$ requires $N = 14.36$ per cent.

The substance is freely soluble in cold pyridine, moderately in cold ether or benzene, and in boiling acetone, chloroform, ethyl acetate, methyl alcohol, and ethyl alcohol, crystallising in minute, snow-white needles. A solution containing 0.1020 gram, in 20 c.c. of dry pyridine, gave $\alpha_D^{20} 15'$ in the 2-dcm. tube, whence $[\alpha]_D^{20} 220.6^\circ$.

Resolution by Acids.—The transformed diazocarbamide is much more resistant towards acids than the original material, being able to withstand the action of boiling acetic acid; moreover, dry hydrogen chloride has no effect on the substance suspended in ether at 20° . Hydrolysis was brought about, however, by warm mixtures of hydrochloric or nitric with glacial acetic acid, and by 50 per cent. sulphuric acid with a few drops of alcohol, benzene-diazonium salt being produced in each case. Owing to an unexpected difficulty, the resulting camphorylphenylcarbamide could not be obtained in crystalline form, the result of neutralising the acid liquid being, in each case, a viscous oil, which was transformed into a hard resin by continued action of aqueous potassium hydroxide. The reason for this was not discovered until an attempt was made to prepare camphorylphenylcarbamide from

aminocamphor and phenylcarbimide (see below), but there was no difficulty in establishing the production of benzenediazonium salt, the diluted solution of hydrolysed diazocarbamide, when filtered from camphorylphenylcarbamide, giving a bulky precipitate of benzeneazo- β -naphthol, which was recrystallised and identified.

Action of Phenylcarbimide on Aminocamphor.

On adding phenylcarbimide to a moderately concentrated ethereal solution of aminocamphor, the resulting action was sufficiently vigorous to boil the solvent; when the odour of isocyanate was no longer perceptible, the honey-like mass deposited on evaporating the ether was dissolved in glacial acetic acid and precipitated with water in order to remove excess of aminocamphor. All attempts to crystallise the substance having failed, we suspected the presence of two isomeric carbamides, similar to those produced by the action of potassium cyanate on aminocamphor hydrochloride (Trans., 1905, **87**, 110), and the oily mixture in the latter case having been transformed into the crystalline ψ -carbamide by the action of hot aqueous potassium hydroxide, the gummy mass from aminocamphor and phenylcarbimide was digested on the water-bath during eight hours with 10 per cent. aqueous potassium hydroxide, treatment which had the desired effect. The hard, friable cake was finely powdered, washed with water, dried in air, and covered with a small quantity of cold methyl alcohol, in which it dissolved freely, but immediately separated in crystals containing one molecule of the solvent. Finally, the substance was recrystallised twice from methyl alcohol, and heated in the steam-oven during twelve hours:

0.2871 gave 25.0 c.c. N_2 at 20° and 763 mm. $N = 10.00$.

$C_{17}H_{22}O_2N_2$ requires $N = 9.78$ per cent.

Camphorylphenyl- ψ -carbamide melts at 152° . It is freely soluble in cold methyl and ethyl alcohols, benzene, chloroform, ethyl acetate, and acetone, but dissolves very sparingly in boiling petroleum, which deposits minute, white needles on cooling; the crystals from methyl alcohol are lustrous, transparent, clear-cut prisms, which become sticky in the desiccator, and retain the solvent after seven days:

0.3859 gave 30.7 c.c. N_2 at 20° and 767 mm. $N = 9.18$.

$C_{17}H_{22}O_2N_2, CH_4O$ requires $N = 8.80$ per cent.

In this form the substance sinters at about 60° , remaining pasty until 90° is reached, when it becomes opaque, and finally melts at 152° .

A solution containing 0.2008 gram (m. p. 152°), made up to

20 c.c. with chloroform, gave α_D $0^{\circ}15'$ in the 2-dcm. tube, whence $[\alpha]_D$ 12.4° , this low figure recalling that of camphoryl- ψ -carbamide (*loc. cit.*). The action of nitrous acid appears to indicate the *pseudo*-form in preference to the normal, giving rise to an unstable nitroso-derivative; this compound will be investigated further, as the product of reduction should be interesting.

Camphoryl o-nitrophenyltriazen (*Camphordiazoamino-o-nitrobenzene*),



Fifteen grams of aminocamphor carbonate were dissolved in dilute acetic acid at zero, treated with 7 grams of *o*-nitroaniline which had been diazotised in a mixture of acetic and hydrochloric acids, and then with excess of crystallised sodium acetate; no precipitation took place until sodium carbonate was added, when the diazoamino-compound separated as a yellow powder. On adding water to a solution of the substance in acetone, golden-yellow leaflets crystallised; the melting point was somewhat indefinite, gas being evolved at about 120° :

0.1115 gave 17.2 c.c. N_2 at 17° and 767.5 mm. $\text{N} = 17.84$.

$\text{C}_{16}\text{H}_{20}\text{O}_3\text{N}_4$ requires $\text{N} = 17.72$ per cent.

The diazoamino-compound is moderately soluble in cold methyl and ethyl alcohols, dissolving freely in acetone, chloroform, benzene, or ethyl acetate; it is only slightly soluble in cold petroleum, and crystallises from the hot solvent in clusters of yellow, lustrous needles. A solution containing 0.1064 gram, made up to 25 c.c. with chloroform, gave $\alpha_D - 2^{\circ}4'$ in the 2-dcm. tube, whence $[\alpha]_D - 242.8^{\circ}$.

Glacial acetic acid dissolves the triazen readily without liberating gas, but on adding one drop of dilute hydrochloric acid to the solution, brisk effervescence sets in; neither with dilute nor concentrated hydrochloric acid was there the slightest indication of a diazonium salt being produced.

Camphoryl-m-nitrophenyltriazen (*Camphordiazoamino-m-nitrobenzene*),



The coupling was effected as in the previous case, and the product separated very slowly in the form of a pale yellow precipitate; the drained substance was dissolved in cold acetone, from which a felted mass of fawn-coloured needles crystallised on dilution with water. After recrystallisation from a mixture of benzene and

petroleum, the melting point was somewhat indefinite, decomposition occurring in the neighbourhood of 122°:

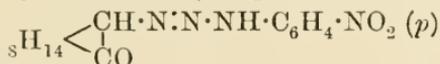
0.1175 gave 18.0 c.c. N₂ at 17° and 764 mm. N=17.87.

C₁₆H₂₀O₃N₄ requires N=17.72 per cent.

The substance is freely soluble in methyl and ethyl alcohols, acetone, chloroform, or ethyl acetate, less readily in benzene; petroleum dissolves it on warming, but not freely, the diazoamino-compound separating in lustrous needles. Cold glacial acetic acid dissolves it very readily without liberating gas, but a minute quantity of mineral acid added to this liquid sets up immediate effervescence. On treating the substance with cold concentrated hydrochloric acid, gas is rapidly liberated, but neither the liquid nor the original substance gives the slightest indication of a condensation product when mixed with an alkaline solution of β-naphthol.

Although the colour of the purified solid is very pale, a solution containing 0.5 gram in 100 c.c. of chloroform was too dark to transmit yellow light in the 2-dcm. tube, and on diluting to 400 c.c., when readings in the polarimeter could be made, no rotation was discernible.

Camphoryl-p-nitrophenyltriazen (Camphordiazoamino-p-nitrobenzene),



Fifty c.c. of aminocamphor hydrochloride solution, containing about 15 grams of the base, were treated with crystallised sodium acetate in excess, and mixed with an acetic acid solution of diazotised *p*-nitroaniline prepared from 6 grams of the base. Precipitation did not take place in the ice-cold liquid until 20 per cent. sodium carbonate had been added in considerable excess, the pale yellow solid being filtered and washed after about one hour in the dark room. The roughly-dried substance was made into a paste with a small quantity of cold acetone, which developed an intense magenta-coloured solution, and freed the compound from associated water; on dissolving the drained material in a further quantity of acetone and diluting with water until crystals appeared, pale yellow, felted needles were obtained, melting at 167° with vigorous intumescence:

0.2058 gave 32.2 c.c. N₂ at 24° and 771 mm. N=17.81.

C₁₆H₂₀O₃N₄ requires N=17.72 per cent.

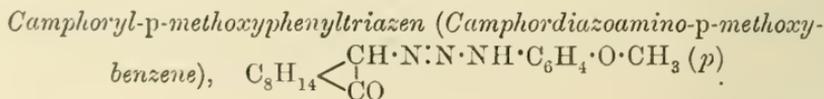
The substance is moderately soluble in cold methyl and ethyl alcohols and in cold acetone, dissolving more freely in ethyl acetate; it is insoluble in petroleum, and only moderately soluble in boiling

benzene, forming a solution which is almost colourless and deposits very pale yellow, lustrous prisms on cooling. When covered with a small proportion of cold pyridine, the substance dissolves, but the liquid sets immediately to a hard mass, no doubt containing pyridine of crystallisation. A solution prepared from 0.1089 gram, made up to 25 c.c. with chloroform, gave α_D 1.00' in the 2-dcm. tube, whence $[\alpha]_D$ 114.8°.

The triazen does not effervesce with cold glacial acetic acid, but it is decomposed immediately by hydrochloric acid; the liquid, however, does not develop a coloration with alkaline β -naphthol. On adding 2 c.c. of concentrated hydrochloric acid to 0.5 gram of the substance suspended in 4 c.c. of glacial acetic acid, steady liberation of gas took place, and a brown solution was formed, yielding an oil on dilution with water; we have failed to identify this product, which always accompanies nitrogen and the appropriate aromatic derivative when the unmethylated triazen derivatives are decomposed by acid, but *p*-nitroaniline was isolated from the acid liquid after removing the camphor residue with ether.

When rubbed with concentrated aqueous potassium hydroxide, the substance becomes pale brown, the colour being destroyed on dilution, but if the triazen is heated with aqueous alkali a faint odour of camphor becomes perceptible, and an intense violet coloration is developed on dilution. These changes are probably due to the formation of an insoluble potassium derivative, which is readily dissociated by water and is decomposed on heating; potassium hydroxide develops a deep red coloration in an alcoholic solution of the triazen, whilst on warming the liquid for a few moments, and then adding water, a very intense but transient violet colour appears.

Unsuccessful attempts have been made to methylate this compound by the action of methyl sulphate in presence of alkali, and by heating with methyl iodide and alcoholic potassium hydroxide or silver oxide. Similar resistance was displayed towards benzoyl chloride.



Ten grams of aminocamphor carbonate were dissolved in dilute acetic acid, and treated with an acid solution of *p*-methoxybenzene-diazonium chloride (from 5 grams of *p*-anisidine), to which considerable excess of crystallised sodium acetate had been added; the liquid remained clear, and even on treatment with sufficient

sodium carbonate to give strong alkalinity there appeared only a turbidity. During twenty-four hours in the ice-chest, however, there separated a pale brown, crystalline precipitate, which was dissolved in cold acetone and reprecipitated with water; on adding light petroleum to the solution in cold benzene, lustrous, colourless, six-sided leaflets crystallised, melting and decomposing at 142° :

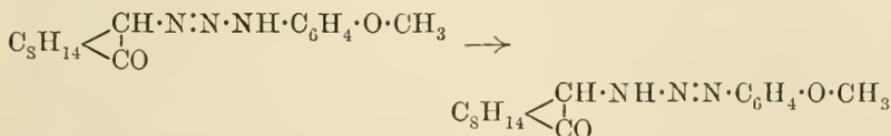
0.2895 gave 0.7217 CO_2 and 0.2020 H_2O . $\text{C} = 67.99$; $\text{H} = 7.75$.

0.1928 „, 24.2 c.c. N_2 at 22° and 765 mm. $\text{N} = 14.31$.

$\text{C}_{17}\text{H}_{23}\text{O}_2\text{N}_3$ requires $\text{C} = 67.77$; $\text{H} = 7.64$; $\text{N} = 13.95$ per cent.

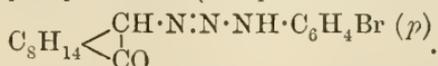
The triazen dissolves freely in acetone or chloroform, less readily in methyl and ethyl alcohols and in benzene; it is moderately soluble in boiling petroleum, from which it crystallises on cooling in colourless, transparent, six-sided plates. A solution containing 0.2100 gram, made up to 25 c.c. with chloroform, gave $\alpha_D^{20} 0^{\circ}50'$ in the 2-dcm. tube, whence $[\alpha]_D^{20} 49.0^{\circ}$.

The behaviour of the substance towards hydrochloric acid is noteworthy. When this agent is added to a solution in glacial acetic acid, gas is liberated immediately, and the product does not give any marked indication of coupling with alkaline β -naphthol, but if the solid material is covered with concentrated hydrochloric acid, there is no perceptible evolution of gas, and after a few minutes' contact, mixing with alkaline β -naphthol develops a bright red coloration; when heated with the acid, gas is set free, and the product also develops colour with alkaline β -naphthol. This experiment suggests that the triazen undergoes limited transformation in the direction:



under the influence of mineral acid at the elevated temperature necessary to effect the normal decomposition; if this explanation is correct, it is not surprising to find the products of decomposing both aryldiazo-groups when diaryltriazens are resolved by hot mineral acids.

Camphoryl-p-bromophenyltriazen (*Camphordiazoamino-p-bromobenzene*),



On adding *p*-bromobenzenediazonium chloride (from 8 grams of *p*-bromoaniline) in dilute acetic acid to aminocamphor carbonate (15 grams), which had been converted into a dilute solution of the acetate, the liquid remained clear until free acid was removed by

sodium carbonate, when a faint turbidity appeared, gradually increasing during twenty-four hours at zero in the dark room; even then the separation of the diazoamino-compound was not complete. The substance was precipitated from cold acetone by adding water, and then recrystallised by diluting the solution in benzene with petroleum, when colourless needles separated, melting and decomposing at 152° :

0.3002 gave 31.25 c.c. N_2 at 20° and 760 mm. $N=11.90$.

$C_{16}H_{20}ON_3Br$ requires $N=12.00$ per cent.

The compound is freely soluble in methyl and ethyl alcohols, acetone, ethyl acetate, or chloroform, less readily in benzene, and only sparingly in boiling petroleum; a solution containing 0.2290 gram, made up to 25 c.c. with chloroform, gave α_D $1.09'$ in the 2-dcm. tube, whence $[\alpha]_D$ 62.7° .

It is not decomposed by concentrated hydrochloric acid until the liquid is warmed, when gas is liberated, but the test for a diazonium salt gave a negative result.

Camphorylphenylmethyltriazen (*Benzenediazomethylaminocamphor*),



Nine grams of methylaminocamphor were suspended in water by adding sodium carbonate to a dilute solution of the hydrochloride, and in presence of much ice, treated with a dilute solution of benzenediazonium chloride prepared from 4 grams of aniline, to which, after diazotisation, considerable excess of a 20 per cent. solution of sodium carbonate had been added. On stirring with crystallised sodium acetate, a pale brown, sticky mass adhered to the glass, so that the liquid from which it separated could be poured away; rubbing with cold alcohol caused the product to become crystalline, and, after drainage, and double repetition of this treatment, the substance was dissolved in cold acetone, from which, on adding water, it crystallised in brilliant, pale brown prisms, melting at 98° without evolving gas:

0.1573 gave 20.4 c.c. N_2 at 17° and 763 mm. $N=15.11$.

$C_{17}H_{23}ON_3$ requires $N=14.74$ per cent.

The triazen is freely soluble in acetone, and dissolves readily in cold alcohol and in petroleum; a solution containing 0.2161 gram, made up to 20 c.c. with chloroform, gave α_D $5.05'$ in the 2-dcm. tube, whence $[\alpha]_D$ 235.2° . In behaviour towards mineral acid it distinguishes itself sharply from the class of triazens just described, being soluble in cold concentrated hydrochloric acid without losing nitrogen, and, on pouring the liquid into an alkaline solution of β -naphthol, the deep red azo-compound is precipitated:

0.1834 gave 0.1612 $C_6H_5 \cdot N_2 \cdot C_{10}H_7O$. $C_6H_5 \cdot N_2 = 37.2$.

0.2464 „ 0.2148 $C_6H_5 \cdot N_2 \cdot C_{10}H_7O$. $C_6H_5 \cdot N_2 = 36.9$.

$C_6H_5 \cdot N_2 \cdot C_{11}H_{15}ON$ requires $C_6H_5 \cdot N_2 = 36.8$ per cent.

The scission by acid is thus practically quantitative, the azo-compound melting at 129° and 133° before and after recrystallisation respectively. The diazonium complex is not eliminated, however, when a solution of camphorylphenylmethyltriazen in dry pyridine containing β -naphthol is heated to the boiling point.

Camphoryl-o-nitrophenylmethyltriazen (o-Nitrobenzenediazomethylaminocamphor), $C_8H_{14} \left\langle \begin{array}{l} CH \cdot N(CH_3) \cdot N : N \cdot C_6H_4 \cdot NO_2 (o) \\ CO \end{array} \right.$.

The coupling proceeded in the expected fashion, the product becoming somewhat sticky during filtration, but returning to the solid state on treatment with a small quantity of cold alcohol; recrystallisation from warm petroleum (b. p. $60-80^\circ$) gave lustrous, yellow needles, melting at 116° without evolving gas:

0.1246 gave 18.8 c.c. N_2 at 18° and 753 mm. $N = 17.26$.

$C_{17}H_{22}O_3N_4$ requires $N = 16.96$ per cent.

The triazen crystallises readily from methyl and ethyl alcohols, being only moderately soluble in the cold media; acetone, benzene, ethyl acetate, and chloroform dissolve it freely, but it is only slightly soluble in cold petroleum. A solution containing 0.2353 gram, made up to 25 c.c. with chloroform, gave $\alpha_D 5^\circ 40'$ in the 2-dcm. tube, whence $[\alpha]_D 301.0^\circ$.

On adding concentrated hydrochloric acid to the pale yellow solution in glacial acetic acid, the colour is immediately destroyed, owing to the formation of the colourless hydrochloride, the stability of which is indicated by the fact that on mixing the liquid with alkaline β -naphthol the colour is very faint; when the dry substance is covered with concentrated hydrochloric acid, it forms a colourless solution, which does not effervesce, but deposits the hydrochloride in crystals, and only after gently warming the liquid is the intense red azo-compound developed with alkaline β -naphthol.

Camphoryl-m-nitrophenylmethyltriazen (m-Nitrobenzenediazomethylaminocamphor), $C_8H_{14} \left\langle \begin{array}{l} CH \cdot N(CH_3) \cdot N : N \cdot C_6H_4 \cdot NO_2 (m) \\ CO \end{array} \right.$.

The initial product of coupling *m*-nitrobenzenediazonium chloride and methylaminocamphor was almost colourless, but became red and sticky during filtration, and after dissolution in cold alcohol crystallised only very slowly; it was necessary to recrystallise the substance several times from alcohol and petroleum, employed

alternately, before the melting point was constant, when lustrous, silky, yellow needles were deposited from the latter solvent, melting at $81-82^\circ$ without evolving gas:

0.1292 gave 19.3 c.c. N_2 at 16° and 751 mm. $N=17.19$.

$C_{17}H_{22}O_3N_4$ requires $N=16.96$ per cent.

The substance is freely soluble in cold acetone, ethyl acetate, chloroform, or benzene, dissolving readily in hot alcohol and in petroleum; although pale yellow in the solid state, the hydrocarbon solutions are colourless. A solution containing 0.1239 gram, made up to 25 c.c. with chloroform, gave $\alpha_D 1^\circ 48'$ in the 2-dcm. tube, whence $[\alpha]_D 181.6^\circ$.

When rubbed with concentrated hydrochloric acid, the compound is transformed into a colourless, gelatinous hydrochloride, which dissolves on being gently warmed; the liquid then develops a deep orange precipitate with alkaline β -naphthol.

Camphoryl-p-nitrophenylmethyltriazen (*p-Nitrobenzenediazomethylaminocamphor*, C_8H_{14} $\left\langle \begin{array}{l} CH \cdot N(CH_3) \cdot N : N \cdot C_6H_4 \cdot NO_2 (p) \\ CO \end{array} \right.$

This compound separated as a yellow, flocculent precipitate on adding sodium carbonate to the mixture of methylaminocamphor and diazonium salt in dilute acetic acid; after crystallisation from dilute acetone, which deposited the substance in pale yellow, silky needles, it melted at 150° without evolving gas:

0.1761 gave 25.7 c.c. N_2 at 20° and 767 mm. $N=16.85$.

$C_{17}H_{22}O_3N_4$ requires $N=16.96$ per cent.

The triazen is freely soluble in cold acetone, chloroform, benzene, or ethyl acetate, less readily in methyl and ethyl alcohols and in hot petroleum, the solution in the last-named being colourless. A solution containing 0.2359 gram, made up to 20 c.c. with chloroform, gave $\alpha_D 7^\circ 20'$ in the 2-dcm. tube, whence $[\alpha]_D 310.8^\circ$.

The yellow solution in glacial acetic acid becomes colourless on adding concentrated hydrochloric acid, but there is no liberation of gas, and, after warming gently, the liquid develops an intense red colour with alkaline β -naphthol:

0.1952 gave 0.1804 $NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_7O$. $NO_2 \cdot C_6H_4 \cdot N_2 = 47.3$.

0.1971 ,, 0.1796 $NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_7O$. $NO_2 \cdot C_6H_4 \cdot N_2 = 46.6$.

$NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_{11}H_{15}ON$ requires $NO_2 \cdot C_6H_4 \cdot N_2 = 45.4$ per cent.

The azo-compound decomposed at 247° and 249° before and after recrystallisation respectively.

Two grams of the *p*-nitro-compound were dissolved in a mixture of glacial acetic and concentrated hydrochloric acids, and heated on the steam-bath until nitrogen ceased to appear; on diluting with water, there separated a crystalline precipitate of *p*-chloro-

nitrobenzene, more of which was obtained by extracting the filtrate with ether. After distillation in steam, the substance melted at 82—83°, whilst the residue in the flask contained a very small quantity of *p*-nitrophenol; methylaminocamphor was recovered from the acid liquid, and identified as the picrate, m. p. 188°.

The pronounced tendency towards salt-formation, which characterises the series of triazen derivatives from methylaminocamphor, and which helps to distinguish them from the class referred to aminocamphor itself, has been studied in the case of the *p*-nitro-compound by adding to an ethereal solution of the triazen sufficient acid dissolved in ether to precipitate the colourless salt, which was then filtered, washed with dry ether, and preserved in the desiccator, where no change in appearance has been observed during the lapse of six months.

The *hydrochloride* melts and decomposes at 146°:

0.2462 gave 0.0959 AgCl. Cl=9.61.

$C_{17}H_{22}O_3N_4 \cdot HCl$ requires Cl=9.66 per cent.

The *sulphate* melts and decomposes at 151°:

0.4185 gave 0.1298 BaSO₄. S=4.25.

$(C_{17}H_{22}O_3N_4)_2 \cdot H_2SO_4$ requires S=4.22 per cent.

The *nitrate* melts and decomposes at 124°:

0.0978 gave 15.2 c.c. N₂ at 18° and 760 mm. N=17.95.

$C_{17}H_{22}O_3N_4 \cdot HNO_3$ requires N=17.81 per cent.

On decomposing these salts with dilute ammonia, unaltered camphoryl-*p*-nitrophenylmethyltriazen was recovered.

Camphoryl-p-methoxyphenylmethyltriazen (*p*-Methoxybenzenediazomethylaminocamphor), $C_8H_{14} \begin{matrix} < \\ \text{CH} \cdot \text{N}(\text{CH}_3) \cdot \text{N} : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_3 \end{matrix} (p)$

The diazoamino-compound separated on adding sodium carbonate to the mixture of diazonium salt and methylaminocamphor, and was crystallised twice from warm dilute alcohol, which deposited flat, lustrous, colourless needles, melting at 74° without evolving gas:

0.1654 gave 19.2 c.c. N₂ at 18° and 763 mm. N=13.46.

$C_{18}H_{25}O_2N_3$ requires N=13.33 per cent.

The substance is freely soluble in all the ordinary organic media, including petroleum; a solution containing 0.1862 gram, made up to 25 c.c. with chloroform, gave α_D 3°28' in the 2-dcm. tube, whence $[\alpha]_D$ 232.7°.

When covered with cold concentrated hydrochloric acid, the compound is immediately dissolved without losing nitrogen, and, on gently warming the liquid and pouring it into alkaline β -naphthol, the intense red azo-compound is produced.

Camphoryl-p-bromophenylmethyltriazen (*p-Bromobenzenediazomethylaminocamphor*), $C_8H_{14} \begin{matrix} < \\ \text{CH} \cdot \text{N}(\text{CH}_3) \cdot \text{N} : \text{N} \cdot \text{C}_6\text{H}_4\text{Br} \text{ (} p \text{)} \\ \text{CO} \end{matrix}$.

Precipitation of the diazoamino-compound from *p*-bromobenzenediazonium chloride and methylaminocamphor in presence of sodium carbonate appeared to be complete after two hours in the dark room; the granular material became somewhat sticky during washing, but was restored to condition by rubbing with cold alcohol. After recrystallisation from this medium, the substance was dissolved in petroleum, which deposited tough, pale pink needles, melting at 112° , along with clear-cut, transparent, colourless prisms, melting at 121° , a mixture of the two modifications melting at 90° . The two forms were sorted by hand, and recrystallised separately without alteration in the temperature of fusion; they gave approximately the same results on analysis:

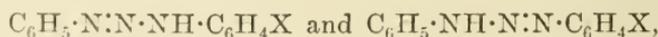
0.4830 (needles) gave 0.2540 AgBr. Br = 22.37.

0.6843 (prisms) gave 0.3556 AgBr. Br = 22.11.

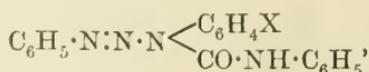
$C_{17}H_{22}ON_3Br$ requires Br = 21.98 per cent.

Both substances dissolve readily in ordinary solvents, and the difference between them was first attributed to dimorphism until it was found that their effects on polarised light are almost antipodal; a solution containing 0.2246 gram (needles, m. p. 112°), made up to 25 c.c. with chloroform, gave $\alpha_D 3^\circ 55'$ in the 2-dcm. tube, whence $[\alpha]_D 218.0^\circ$, whilst 0.2253 gram (prisms, m. p. 121°), under similar conditions, gave $\alpha_D -4^\circ 17'$, corresponding to $[\alpha]_D -232.1^\circ$. In spite of this remarkable difference, the two substances behave alike towards hydrochloric acid, undergoing the resolution characterising this class of triazens, and consequently developing an intense red colour when the diluted liquid is poured into alkaline β -naphthol.

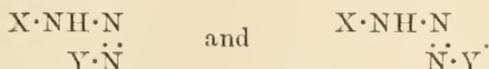
It is noteworthy that the investigation of bromodiazobenzenes in the hands of Hantzsch and F. M. Perkin (*Ber.*, 1897, 30, 1394) brought to light a pair of modifications behaving alike in every chemical respect, but differing from one another in melting point; a similar phenomenon was noticed in connexion with the *p*-chloro-derivative, but not among the nitro-compounds. The explanation to which Hantzsch and Perkin were impelled represented the normal and abnormal (lower melting) forms by the expressions:



and although phenylcarbimide furnished in each case the same diazocarbamide,



it was supposed that the agent, previously to combination, transformed the labile, more fusible modification into the "normal" isomeride (*loc. cit.*, 1406). It will be noticed, however, that in the case of camphoryl-*p*-bromophenylmethyltriazen, this explanation would not apply, there being no available hydrogen in the triazen chain; moreover, both forms give diazonium salt on treatment with acid, behaviour which eliminates the possibility of the methyl group having wandered. We hope to return to this subject later, because there are two remaining contingencies to be considered. It might be that in these halogen derivatives of the triazen nucleus, cases have been brought to light in which isomerism of the type encountered among the oximes has been realised, represented by the formulæ:



The alternative explanation would apply to the camphoryl-triazens, but not to the benzenoid ones, and depends on the fact that aminocamphor and methylaminocamphor, arising by reduction of *isonitrosocamphor* and its *N*-methyl ether respectively, should occur in two forms, *cis* and *trans*, corresponding with bornylamine and neobornylamine from camphoroxime. Only one form has yet been noticed, and there seems to be no particular reason why, among the numerous changes to which these bases and their derivatives have been submitted, coupling with *p*-bromobenzene-diazonium chloride should exert such marked selective action.

As in the case of the *p*-nitro-compound, salts were prepared from the modification of camphoryl-*p*-bromophenylmethyltriazen which melts at 112°.

The *hydrochloride* melts and decomposes at 130°:

0.2859 gave 0.0995 AgCl. Cl = 8.59.

$\text{C}_{17}\text{H}_{22}\text{ON}_3\text{Br}\cdot\text{HCl}$ requires Cl = 8.84 per cent.

The *sulphate* melts and decomposes at 153°:

0.5878 gave 0.1638 BaSO₄. S = 3.83.

$(\text{C}_{17}\text{H}_{22}\text{ON}_3\text{Br})_2\cdot\text{H}_2\text{SO}_4$ requires S = 3.87 per cent.

The *nitrate* melts and decomposes at 137°:

0.1448 gave 16.8 c.c. N₂ at 17° and 763 mm. N = 13.52.

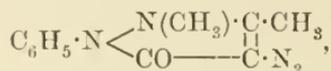
$\text{C}_{17}\text{H}_{22}\text{ON}_3\text{Br}\cdot\text{HNO}_3$ requires N = 13.11 per cent.

On decomposing these salts with aqueous sodium carbonate, the original triazen (m. p. 112°) was recovered.

CCXXV.—*The Triazo-group. Part X. Triazoantipyrine.*

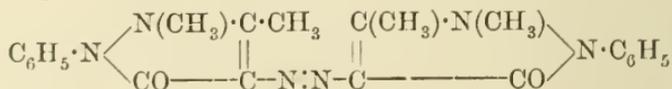
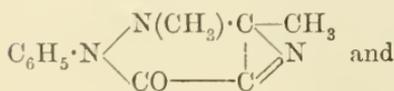
By MARTIN ONSLOW FORSTER and ROBERT MÜLLER.

RECOGNISING that 4-triazo-1-phenyl-2:3-dimethylpyrazolone (triazoantipyrine),



would present a type of triazoketone distinct from those which have been already investigated (Trans., 1905, **87**, 826; 1908, **93**, 72 and 669), we prepared the substance by the action of hydrazoic acid on antipyrildiazonium sulphate. The structural features which give it interest are, in the first place, absence of hydrogen from the neighbourhood of the triazo-group, with the consequent uncertainty as to the behaviour of this complex under the influence of carbonyl in the ortho-position, and, secondly, the unsaturated linking by which the triazotised carbon atom is associated with the next member of the ring.

The former of these peculiarities no doubt underlies the indifference of triazoantipyrine towards alkali, which does not liberate two-thirds of the azidic nitrogen, and thus distinguishes the substance from those ketonic azoimides which possess the group $\text{N}_3 \cdot \text{CH} \cdot \text{CO}$ in common. The most conspicuous property of triazoantipyrine, however, is the spontaneous loss of nitrogen which occurs in the crystalline material with lapse of time, an alteration which takes place very rapidly in the dissolved state, the straw-coloured liquid quickly becoming deep red. It has not been possible to characterise the resulting azoantipyrine very sharply, but as the change in question is an unusual point in the chemistry of the triazo-group, we think it deserves to be recorded. The choice between the formulæ:



for azoantipyrine cannot be made decisively, because all attempts to crystallise the substance have failed, and therefore we do not feel justified in attaching importance to the determinations of molecular weight. Although the second expression would be in conventional accordance with the structure of benzenoid azo-compounds, the production of 1-hydroxy-5-phenyltetrazole from

the hypothetical benzhydroximic azide (this vol., 184; compare also Wieland, *Ber.*, 1909, **42**, 4199):



so far resembles the rearrangement involved in the change:



as to bring the simpler constitution within the range of probability. On the other hand, it is reasonable to suppose that the bicyclic structure just represented, in which an osotriazole ring is associated with a pyrazolone, would not be so unstable as to suffer immediate loss of nitrogen, and this circumstance, in conjunction with the colour of the substance and its amorphism, incline us to prefer the constitutional formula which is analogous to that of azobenzene.

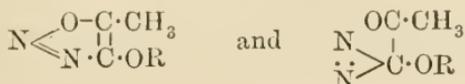
Somewhat indirectly, perhaps, the present subject bears on the mechanism of diazotisation, inasmuch as it adds one more to the small, but significant, group of facts which go to show that the change in question is not confined to benzenoid substances. The observation that aminoantipyrine may be diazotised under conditions similar to those attending the production of benzenediazonium salts was made several years ago (Knorr and Stolz, *Annalen*, 1896, **293**, 68), but does not appear to have received the attention it deserves in connexion with the constitution of diazonium salts. Among other non-benzenoid cyclic systems known to furnish diazonium salts may be mentioned the triazole and tetronic acid rings, Thiele and Manchot (*Annalen*, 1898, **303**, 33) having shown that aminotriazole and aminomethyltriazole:



behave like aniline towards nitrous acid, whilst Wolff and Lüttringhaus (*Annalen*, 1900, **312**, 133) transformed aminotetronic acid into a diazo-oxide:

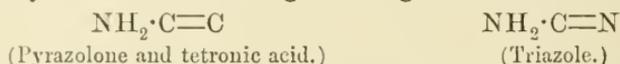


which develops a colouring matter with alkaline α -naphthol. Moreover, other diazoanhydrides, described by Wolff and his collaborators (*Annalen*, 1902, **325**, 129), have been represented as arising from aliphatic amines, but although the author quoted regards these compounds as analogous to the diazo-oxide from tetronic acid, the latter of the two formulæ:

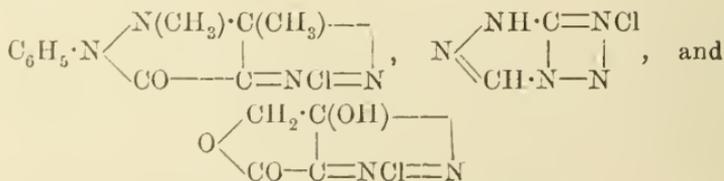


must, in the opinion of many chemists, be regarded as agreeing more completely with the properties of the substances, and has the advantage of bringing them into line with ethyl diazoacetate.

Excluding these somewhat doubtful substances, therefore, three well-established cases remain in which a non-benzenoid cyclic system has been transformed into a diazonium salt, and an attempt must be made to bring the fact into harmony with the more familiar occurrences of diazotisation, particularly since Cain's theory (Trans., 1907, **91**, 1049) has lifted into greater prominence the seeming dependence of the diazonium structure on a benzenoid host. From this standpoint it is noteworthy that in the amino-compounds derived from the pyrazolone, triazole, and tetric acid rings, the immediate environment of the diazotisable nitrogen is to this extent similar, that the carbon atom which carries the amino-group is doubly linked with a neighbouring member of the ring system:



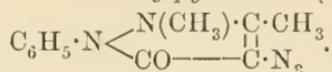
The underlying principle of Cain's theory is recognition of the possibility that diazonium salt formation involves participation of the carbon atom in the para-position with respect to the amino-group, and the consequent production of a hemi-quinone. The exclusion of this possibility in the case of the five-membered ring-systems under discussion leads apparently to one of two alternatives, either the abandonment of Cain's theory, or the adoption of the extension thereto proposed by Morgan and Micklethwait (Trans., 1908, **93**, 617). Of these conclusions, we prefer the latter. There is so much to be said in favour of regarding diazotisation as depending on the residual affinity of the complex to which the amino-group is attached that a return to Blomstrand's formula seems retrograde. The adroit inclusion of the ortho-position by Morgan and Micklethwait would render diazotisable those amino-derivatives of rings in which a double linking associates the ortho-member. In the benzenoid series, the participation of the ortho-position is doubtless one phase only; in the diazonium salts of pyrazolone, tetrazole, and tetric acid derivatives, it is probably static, the formulæ:



representing the diazonium chlorides, respectively.

EXPERIMENTAL.

4-Triazo-1-phenyl-2:3-dimethylpyrazolone (Triazoantipyryne),



Aminoantipyryne sulphate was prepared by hydrolysing the benzylidene compound (8·8 grams), suspended in ether, with aqueous sulphuric acid (6 grams diluted to 50 c.c.), and freed from benzaldehyde by two subsequent extractions; ether having been removed from the acid liquid, this was transferred to the dark room, diazotised, and treated with excess of sodium azide (2·5 grams instead of 1·95). Vigorous effervescence ensued, and in presence of a large proportion of crushed ice the triazo-compound separated in pale yellow leaflets, insufficient cooling leading to an oil which rapidly solidified. The roughly-dried substance was dissolved without delay in cold benzene, with which it appears to combine, the solution being diluted with petroleum, when lustrous, flat, straw-coloured crystals were deposited, sometimes attaining an inch in length; on transferring the substance to porous earthenware, it rapidly lost its lustre, and melted at 74° to a deep red, effervescent liquid:

0·0985 gave 0·2079 CO₂ and 0·0448 H₂O. C=57·56; H=5·05.

0·0915 „, 24·6 c.c. N₂ at 20° and 768 mm. N=31·09.

C₁₁H₁₁ON₅ requires C=57·64; H=4·80; N=30·56 per cent.

Triazoantipyryne dissolves readily in methyl and ethyl alcohols, benzene, and acetone, but is insoluble in cold petroleum. Interaction with sulphuric acid is very violent, being almost explosive when the concentrated agent is used; yellow fumes are liberated, and a black tar produced. Even 50 per cent. acid brings about vigorous decomposition, but by reducing the strength to 25 per cent., it is possible to measure the gas set free, two-thirds the azidic nitrogen being evolved:

0·1293 gave 13·2 c.c. N₂ at 17° and 776 mm. N=12·10.

C₁₁H₁₁ON₅ requires $\frac{2}{3}$ N=12·22 per cent.

The triazo-compound loses nitrogen also when treated with stannous chloride in hydrochloric acid, but in this case variable results are obtained, and it is not possible to follow the reaction quantitatively. Ammoniacal silver oxide is reduced very readily by the substance, a mirror being deposited on raising the temperature. On adding aqueous potassium hydroxide to an alcoholic solution of triazoantipyryne, the behaviour of the substance is found to be quite different from that of triazoketones in which hydrogen

is attached to the carbon atom carrying the azoimide complex, and the usual stormy liberation of nitrogen does not occur.

Azoantipyryne,



If the crystallised triazoantipyryne is allowed to remain suspended in the mother liquor, a remarkable alteration sets in, even when light is excluded. The crystals lose their brilliancy, changing to a red powder, whilst the liquid, originally clear and pale yellow, becomes red and turbid, evolving gas.

This decomposition was accelerated and completed by maintaining the liquid at 40—50° during eight to ten hours, when the red powder was filtered, dissolved in benzene, precipitated by petroleum, redissolved in chloroform, and reprecipitated by ethyl acetate. The dull red powder became dark red and slimy when spread on earthenware, but if left on the filter-paper and allowed to dry by exposure to air, the paler colour and powdery condition persisted, and the substance intumescenced a few degrees above 165°, at which temperature it suddenly became dark red:

0.1019 gave 18.2 c.c. N₂ at 17° and 770 mm. N = 21.00.

C₂₂H₂₂O₂N₆ requires N = 20.90 per cent.

The behaviour of the substance towards concentrated sulphuric acid, stannous chloride, and ammoniacal silver oxide was negative. Picric acid, when added to an alcoholic solution, gave a dark red precipitate, but this immediately became sticky, and could not be crystallised. The azo-compound is readily soluble in chloroform, pyridine, and the alcohols, being sparingly dissolved by ethyl acetate and by hot petroleum; the behaviour towards benzene is curious, for when the substance is covered with a small proportion of the cold hydrocarbon a deep red solution is formed, but becomes turbid on further addition of the solvent. It has not been possible to crystallise the compound, but a specimen obtained by allowing crystallised triazoantipyryne to undergo spontaneous decomposition in a stoppered vessel was found to have retained the crystalline form of the original material, although quite red and containing only 21 per cent. of nitrogen. On account of the difficulties indicated, we do not place much reliance on the determinations of molecular weight; these varied considerably between 300 and 400, the latter figure being required by the molecular formula for azoantipyryne.



© 1880 A. S. DREYER & CO.

S. Mandeville

MENDELÉEFF MEMORIAL LECTURE.

DELIVERED ON OCTOBER 21ST, 1909.

By W. A. TILDEN, D.Sc., LL.D., F.R.S., Past-President of the
Chemical Society.

To many of the present generation of English chemists, the commanding, patriarchal figure of Mendeléeff was quite familiar. Though his several visits to London were often connected with official business of the Russian Government Department of Weights and Measures, of which he was the chief official during the later years of his life, he came several times with more purely scientific objects. In 1889 the occasion of his presence in London was the Faraday Lecture which he had been invited to give to the Chemical Society, but which, owing to a sudden and urgent recall to his home, he was unable to deliver in person. His last appearance in this country was in November, 1905, when the Copley Medal was awarded to him by the Royal Society.

The Chemical Society can see his face no more, and all that it can now do is to inscribe high on its roll of honour the name which, more than any other, will be for ever associated with the development of the great generalisation known as the periodic system of the elements.

Dmitri Ivanovitsch Mendeléeff * was the fourteenth and youngest child of his parents, Ivan Pavlovitsch and Maria Dmitrievna, *née* Kornileff. His father, a former student of the Chief Pedagogic Institute of St. Petersburg, obtained the appointment of Director of the Gymnasium at Tobolsk, in Siberia, where he met Maria Dmitrievna, who became his wife. After a few years at Tobolsk, he was transferred to school directorships in Russia, first at Tambov, and afterwards at Saratov. But in order to satisfy the ardent wish of his wife, he took advantage of an opportunity of exchange, by which he became once more Director of the College at Tobolsk, and the family returned to Siberia. Here on January 27th, 1834 (O.S.) was born Dmitri Ivanovitsch, the youngest son.

* For many of the details of Mendeléeff's career and of his home life the writer is indebted to the family chronicle compiled, soon after his death, by his niece, N. J. Gubkina (*née* Kapustina), and published in St. Petersburg, also to pamphlets by A. Archangelsky and P. J. Robinowitsch. He also desires to express his thanks to Mr. D. V. Jéquier, of St. Petersburg, as well as to several Russian friends, for valuable assistance in translation.

Soon after his birth the father became gradually blind from cataract in both eyes, and was obliged to resign, the whole family, including eight children, having to subsist on a small pension of 1000 roubles (about £100 per annum). The mother, Maria Dmitrievna, belonged to the old Russian family, Kornileff, settled at Tobolsk. They were the first to establish in Siberia the manufacture of paper and glass. In 1787 the grandfather of Dmitri opened at Tobolsk the first printing press, and from 1789 produced the first newspaper in Siberia, the *Irtysch*. The glass works were situated in the village of Aremziansk, a short distance from Tobolsk.

According to the family tradition, one of the Kornileffs in a previous generation had married a Khirgis Tartar beauty, whom he loved so passionately that when she died he also died of grief. The pure Russian blood thus received a strain of the Mongolian race, and some of their descendants preserved traces of the Oriental type. This, however, was not very noticeable in the features of the chemist.

From her childhood, Maria Dmitrievna was distinguished by her intelligent wish for instruction, and having no other resource when her brother Basile went to school she repeated by herself all his lessons, and thus, unaided, obtained some part of the knowledge so eagerly desired. There can be no doubt she was a woman possessed of remarkable vigour of mind, who exercised great influence over her children. Her activity and capacity are further illustrated by the fact that when her husband became blind she revived the business of the glass works, and carried it on till after his death from consumption in 1847.

Tobolsk was at that time a place of banishment for many political exiles, the so-called Decembrists, one of whom, Bassargin, married Olga, an elder sister of Dmitri. To these Decembrists the boy owed his first interest in natural science. His mother had always cherished the hope that at least one of her children would devote himself to science, and accordingly, after her husband's death and the destruction of the glass works by fire, and spite of failing health and scanty means, she undertook the long and tedious journey from Tobolsk to Moscow, accompanied by her remaining children, Elizabeth and Dmitri Ivanovitsch, with the object of entering the latter, then nearly fifteen years of age, at the University. Disappointed in this object, owing to official difficulties, she removed in the spring of 1850 to St. Petersburg, where ultimately, with the assistance of the Director, Pletnoff, of the Central Pedagogic Institute, a friend of her late husband, she succeeded in securing for her son admission to the Physico-

Mathematical Faculty of the Institute, together with much-needed pecuniary assistance from the Government.

The debt which Dmitri Ivanovitsch owed to his mother he acknowledged later in the introduction to his work on "Solutions," which he dedicated to her memory in the following interesting lines:

"This investigation is dedicated to the memory of a mother by her youngest offspring. Conducting a factory, she could educate him only by her own work. She instructed by example, corrected with love, and in order to devote him to science she left Siberia with him, spending thus her last resources and strength. When dying, she said, 'Refrain from illusions, insist on work, and not on words. Patiently search divine and scientific truth.' She understood how often dialectical methods deceive, how much there is still to be learned, and how, with the aid of science without violence, with love but firmness, all superstition, untruth, and error are removed, bringing in their stead the safety of discovered truth, freedom for further development, general welfare, and inward happiness. Dmitri Mendeléeff regards as sacred a mother's dying words. October, 1887."

In the Pedagogic Institute Dmitri Ivanovitsch was thus able to devote himself to the mathematical and physical sciences under the guidance of Professors Leng and Kupfer in physics, Voskresensky in chemistry, and Ostragradsky in mathematics. Unfortunately, at the end of his course, his health failed, and about this time his mother died. Having been ordered to the South, he fortunately obtained an appointment as chief science master at Simferopol, in the Crimea. The southern climate soon alleviated the serious symptoms of lung disorder, and removal being necessary in consequence of the Crimean War, he was able soon afterwards to undertake a post as teacher of mathematics and physics at the Gymnasium at Odessa. In 1856 he returned to St. Petersburg, and at the early age of twenty-two he was appointed *privat docent* in the University, having secured his certificate as master in chemistry.

At this time he appears to have passed rapidly from one subject to another, but he soon found matter for serious and protracted study in the physical properties of liquids, especially in their expansion by heat. And when, in 1859, by permission of the Minister of Public Instruction Mendeléeff proceeded to study under Regnault in Paris and afterwards in Heidelberg, he devoted himself to this work, communicating his results to Liebig's *Annalen* and the French Academy of Sciences. Returning two years later to St. Petersburg, he secured his Doctorate, and was soon after-

wards appointed Professor of Chemistry in the Technological Institute. In 1866 he became Professor of General Chemistry in the University, Butlerow at the same time occupying the Chair of Organic Chemistry.

As a teacher, Mendeléeff seems to have possessed a special talent for rousing a desire for knowledge, and his lecture room was often filled with students from all faculties of the University. Many of his former students remember gratefully the influence he exercised over them.* One of these writes: "I was a student in the Technological Institute from 1867 to 1869. Mendeléeff was our professor, and in 1868 taught organic chemistry. The previous course by the professor of inorganic chemistry consisted of a collection of recipes, very hard to remember, but, thanks to Mendeléeff, I began to perceive that chemistry was really a science. The most remarkable thing at his lectures was that the mind of his audience worked with his, foreseeing the conclusions he might arrive at, and feeling happy when he did reach these conclusions. More than once he said, 'I do not wish to cram you with facts, but I want you to be able to read chemical treatises and other literature, to be able to analyse them, and, in fact, to understand chemistry. And you should remember that hypotheses are not theories. By a theory I mean a conclusion drawn from the accumulated facts we now possess which enables us to foresee new facts which we do not yet know.' He was considered among the students a most liberal man, and they thought of him as a comrade. More than once during a disturbance between the students and the administration Mendeléeff supported the students, and under his influence many matters were put right." (L. G.) Another former student in the University writes as follows: "I am sorry to say I did not know Mendeléeff personally. I only had the good fortune to follow, in the years 1867-69, his lectures on both Organic and Inorganic Chemistry. The former was an abridged course, which he had the admirable idea to deliver for us students of the mathematical branch of the physico-mathematical faculty. He reduced this course of one lecture a week during one year to a general review of organic compounds and the general laws of their structure. You can imagine what it must have been in the hands of Mendeléeff, thirty-three or thirty-four years old at that time, in the full enjoyment of his mental powers, and just then plunged into the study of his great generalisations. For me it was a revelation, being occupied with the great questions connected with the development of the new system of atomic weights,

* For the following reminiscences, the writer is indebted to Mr. L. Goldenberg and Prince P. Kropotkin respectively.

the mechanical theory of heat, etc. Grove's, Thomson's, Joule's, Séguin's works were then just out, and in these years a sudden blossoming of the natural sciences in all directions seemed to bring us near to the solution of the great problems of the nature of matter and of gravitation. Then I followed Mendeléeff's lectures on Inorganic Chemistry. The 'Principles of Chemistry' was not yet out, but he was evidently writing it at that time. You know how much is said in the footnotes to his 'Principles'; well, imagine each of these notes developed into a beautiful improvisation, with all the freshness of thought of a man who, while he speaks, evolves all the arguments for and against, there on the spot. The hall was always crowded with something like two hundred students, many of whom, I am afraid, could not follow Mendeléeff, but for the few of us who could it was a stimulant to the intellect and a lesson in scientific thinking which must have left deep traces in their development, as it did in mine." (P. K.)

One of Mendeléeff's most remarkable personal features was his flowing abundance of hair. The story goes that, before he was presented to the late Emperor, Alexander III., his Majesty was curious to know whether the professor would have his hair cut. This, however, was not done, and he appeared at Court without passing under the hands of the barber. His habit was to cut his hair once a year in spring, before the warm weather set in. His eyes, though rather deep set, were bright blue, and to the end of his life retained their penetrating glance. Tall in stature, though with slightly stooping shoulders, his hands noticeable for their fine form and expressive gestures, the whole figure proclaimed the grand Russian of the province of Tver.

At home, Mendeléeff always wore an easy garment of his own design, something like a Norfolk jacket without a belt, of dark grey cloth. He rarely wore uniform or evening coat, and attached no importance to ribbons and decorations, of which he had many.

As to his views on social and political questions, many people thought him a rigid monarchist, but he said of himself that he was an evolutionist of peaceable type, desiring a new religion, of which the characteristic should be subordination of the individual to the general good. He always viewed with much sympathy what is called the feminine question. At the Office of Weights and Measures, he employed several ladies, and about 1870 he gave lectures on chemistry to classes of ladies. Nevertheless he considered women inferior to men both in business and in intellectual pursuits, and he thought the chief promoters of the feminine movement aimed, not so much at equality of political position, as at opportunities for work and to escape inactivity. But he thought

the feminine temperament specially suited to all branches of art in the broadest sense of the word, including education.

Mendeléeff held decided views on the subject of education, which he set forth in several publications, especially "Remarks on Public Instruction in Russia" (1901). Here he says, "The fundamental direction of Russian education should be living and real, not based on dead languages, grammatical rules, and dialectical discussions, which, without experimental control, bring self-deceit, illusion, presumption, and selfishness." Believing in the soothing effect of a vital realism in schools, he considered that universal peace and the brotherhood of nations could only be brought about by the operation of this principle. Speaking of the reforms desirable, he says that "for such reforms are required many strong realists; classicists are only fit to be landowners, capitalists, civil servants, men of letters critics, describing and discussing, but helping only indirectly the cause of popular needs. We could live at the present day without a Plato, but a double number of Newtons is required to discover the secrets of nature, and to bring life into harmony with the laws of nature." Mendeléeff was evidently a philosopher of the same type as our own Francis Bacon.

"I am not afraid," he says later, "of the admission of foreign, even of socialistic, ideas into Russia, because I have faith in the Russian people, who have already got rid of the Tartar domination and the feudal system."

Mendeléeff always dined at six o'clock, and liked to entertain his friends and relations, but in his own diet he was extremely moderate. After dinner he enjoyed reading light literature, especially books of adventure, such as those of Fenimore Cooper or Jules Verne. But his literary tastes were peculiar. Though interested in serious literature and appreciating Shakespeare, Schiller, Goethe, Victor Hugo, and Byron as well as the Russian classics, beginning with Zhoucovsky and Pouschkin, his favourites among Russian poets were Maïcoff and Tutcheff, and among the rest Byron. Of the last-named he preferred to all his other works the gloomy poem called "Darkness," and among the rest the "Silentium" of Tutcheff.

He rarely went to the theatre, and did not approve of frequent visits to the theatre by his children, as he considered such distractions tend to destroy concentration and fill the mind with "trifles and foolishness." On the other hand, he was very fond of pictures, and he visited all the exhibitions. That he was interested in questions relating to art, and had given much thought to æsthetic problems, is indicated by a letter* which he addressed in November, 1880, to the well-known Russian daily paper of that time,

* Considerably condensed in the following abstract.

Goloss (The Voice), on the subject of a picture by Kouindji, "Night in the Ukraine." Writing of the influence of landscape on different minds, he says, "At first it seemed to me a matter of personal taste, of individual sensitiveness of different persons to the beauty of nature." But, rejecting this simple view, he was led to a conception which he regarded as really satisfactory, and which he wished to share with others. He says, "Landscape was depicted in antiquity, but was not in favour in those times. Even the great masters of the sixteenth century made use of it merely as a frame to their pictures. It was the human form which principally inspired artists of that epoch; even the gods and the Almighty Himself appeared to their minds in human shape. In this alone they found the infinite, the inspiring, the divine. And this was because they worshipped human mind and human spirit. This found expression in science in an exceptional development of mathematics, logic, metaphysics, and politics. Later, however, men lost faith in the absolute and original power of human reason, and they discovered that the study of external nature assists even in the correct appreciation of the nature of the human inner self. Thus nature became an object of study; a natural science arose unknown either to antiquity or to the period of the Renaissance. Observation and experience, inductive reasoning, submission to the inevitable, soon gave rise to a new and more powerful, more productive method of seeking truth. It thus became evident that human nature, including its consciousness and reason, is merely a part of the whole, which is easier to comprehend as such from the study of external nature than of the inner man. External nature thus ceased to be merely subservient to man, and became his equal, his friend. Dead and senseless as it had been, it now became alive. Everywhere it presented motion, stores of energy, natural reason, simplicity, and plan. Inductive and experimental science became a crown of knowledge, royal metaphysics and mathematics had now to be content with modest questioning of nature. Landscape painting was born simultaneously with this change, or perhaps a little earlier. Thus it will probably come to pass that our age will hereafter be known as the epoch of natural science in philosophy, and of landscape in art. Both derive their materials from sources external to man. . . . Man has, however, not been lost sight of as an object of study and of artistic creation, but he now appears, not as a potentate or as a microcosm, but merely as part of a complex whole."

In 1863, when twenty-nine years of age, Mendeléeff married his first wife, *née* Lestshoff, by whom he had one son, Vladimir,* and a daughter, Olga; but the marriage proved unhappy, and after

* Died in 1899, aged 34.

living apart for some time there was a divorce. In 1877 he fell in love with a young lady artist, Anna Ivanovna Popova, of Cossack origin, and in 1881 they were married. This lady exercised considerable influence over his views about art, and the walls of his study were furnished with many products of her pencil, notably portraits of Lavoisier, Descartes, Newton, Galileo, Copernicus, Graham, Mitscherlich, Rose, Chevreul, Faraday, Berthelot, and Dumas, and others of relatives. After his second marriage, Mendeléeff lived first at the University, and afterwards in the apartments built for the Director at the Bureau of Weights and Measures, and here his younger children were born, Lioubov (Aimée), Ivan (Jean), and the twins, Maria and Vassili (Basile).

In 1890, in consequence of a difference with the administration, Mendeléeff retired from the Professorship in the University. During the disturbances among the students in that year, he succeeded in pacifying them by promising to present their petition to the Minister of Education. Instead of thanks for this service, however, the Professor received a sharp reprimand from the authorities for not minding his own business. The consequence was that Mendeléeff resigned. Independently of the petition, however, there were probably deeper reasons for his being out of favour with the Ministry, connected with his irreconcilable enmity to the classical system of education already referred to (p. 2082). Of this he had made no secret, and it had already brought him into conflict with the authorities. In 1893, however, he was appointed by M. Witte to the office of Director of the Bureau of Weights and Measures, which he retained till his death.

In the earlier part of his life, Mendeléeff was interested in carrying on a series of agricultural experiments on his Tver estate, Boblovo. The peasants, much struck by his success and the abundance of his crops, inquired of him whether this was due to his luck or to his "talent." With a smile and the patois which he always affected in speaking to the country people, he informed them that he certainly had "talent," and, as he said afterwards at home, there is no merit in having luck.

Once during the solar eclipse in 1887 he ascended alone in a balloon with the object of making scientific observations. His assistant, Kovanko, who sat with him in the basket, alighted at the last moment, probably ordered to do so by his chief because the balloon would not rise. When the balloon shot up quickly and disappeared in the clouds, his family was naturally very much alarmed. Fortunately the hero of the adventure was able to descend safely, and a few hours later returned to his family from Moscow. The peasant women thereafter used to tell that Dmitri

Ivanovitch flew on a bubble and pierced the sky, and for this the authorities made him a chemist!

Mendeléeff was very democratic in his habits, and when travelling from the Capital to his estate, six or seven hours by rail, he always made use of the third class, and on the way talked freely to his fellow-passengers on all sorts of subjects, so that at the end of the journey he was surrounded by all sorts of people. At the railway station, about twelve miles from Boblovo, he was always met by the same driver, Zassorin, who with his troika of greys transported the whole family at full gallop, according to Russian custom.

Such, then, are the chief features of a great personality. If it be admitted that stories are told of his occasional irritability of temper, we can well place on the other side of the account the cordial relations always subsisting between the Professor and his assistants, the confidence and respect between the Master and his servants, the deep affection between the Father and his children, which are known to have persisted throughout his life, and which could be illustrated by many anecdotes. These stories merely serve "to give the world assurance of a man."

For us who live on the other side of Europe, separated as we are by race, by language, by national and social customs, and by form of government, it is not easy to understand completely the texture of such a mind, the quality of such genius, and the conditions, social or political, which may have served to encourage or to repress its activity. The Russian language may be eloquent, expressive, versatile, and harmonious, or it may possess any other good quality that may be claimed for it by those to whom it is a mother tongue, but the fact remains that it is a barrier to free intercourse between the Russian people and the world outside the Russian Empire. This alone creates a condition which must influence the development of thought, and must give to Russian science and philosophy a colour of its own. Mendeléeff was, like many educated Russians, a man of very liberal views on such subjects as education, the position of women, on art and science, and probably on national government. We can hardly guess what would be the influence on such a nature of a rigid administrative *régime* which forbids even the discussion of such questions. We in England are almost unable to imagine such a state of things as would be represented by the closing of, say, University College for a year or more, because the question whether the House of Lords ought to be abolished had been debated in the Students' Union. Imagine the Professor of Chemistry, along with his colleagues, for such a reason deprived of the use of his laboratory

by the police, and only allowed to resume his studies when someone down at Scotland Yard thought proper. Such being the experience of most of the Russian Universities and Technical High Schools, it is not surprising that the output of Russian science, notwithstanding the acknowledged genius of the Russian people, appears sometimes comparatively small. The amount of work done by Mendeléeff, both experimental and theoretical, was prodigious, and all the more remarkable considering the cloudy atmosphere under which so much of it was accomplished.*

In 1882 the Royal Society conferred on Mendeléeff, jointly with Lothar Meyer, the Davy Medal. In 1883 the Chemical Society elected him an Honorary Member, and in 1889 it conferred upon him the highest distinction in its power to award, namely, the Faraday Lectureship, with which is associated the Faraday Medal. In 1890 he was elected a Foreign Member of the Royal Society, and in 1905 he received the Copley Medal. So far as England is concerned, his services to science received full acknowledgment. It is all the more remarkable, therefore, that he never became a member of the Imperial Academy of Sciences of St. Petersburg.

Towards the end of 1906 Mendeléeff's health began to fail. Nevertheless he was able to attend the Minister on the occasion of an official visit in January to the office of Weights and Measures, but he caught cold and, enfeebled as he had been by influenza in the preceding autumn, inflammation of the lungs set in. Retaining consciousness almost to the last, he requested even on the day of his death to be read to from the "Journey to the North Pole," by his favourite author, Jules Verne. He died in the early morning of the 20th January (O.S.), 1907, within a few days of his seventy-third birthday. He was buried in the Wolkowo Cemetery beside the graves of his mother and son.

Turning now to a survey of Mendeléeff's work as a man of science, it will be sufficient if we pass lightly over his first essays. Like so many other chemists, he began by handling simple questions of fact, his first paper, dated 1854, when he was twenty years of age, being on the composition of certain specimens of orthite. It was not till 1859 that he settled down to serious examination of the physical properties of liquids, which led him to a long series of experiments on the thermal dilatation of liquids, of which the

* Professor Walden, at the end of a biographical notice recently published in the *Berichte d. Deut. Chem. Ges.*, April, 1909, gives a list of 262 printed publications by Mendeléeff. These include, not only memoirs on physical and chemical subjects, but books, pamphlets, reports, and newspaper articles relating to exhibitions, to the industries of Russia, to weights and measures, to education, to art, and even to spiritualism.

chief ultimate outcome was the establishment of a simple expression for the expansion of liquids between 0° and the boiling point (Trans., 1883, 45, 126). This formula is liable to the same kind of modification which has been found necessary in the case of gases. It is, of course, applicable only to an ideal liquid from which all known liquids differ by reason of differences of chemical constitution and consequent differences of density, viscosity, and other properties. Thorpe and Rücker, by applying van der Waals' theory of the general relation between the pressure, volume, and temperature of bodies to Mendeléeff's expression for the thermal expansion, developed a simple method of calculating the critical temperature of liquids from observations of their expansion (Trans., 1884, 45, 135).

Mendeléeff devoted a large amount of time and of experimental skill to the estimation of the densities of various solutions, especially mixtures of alcohol and water and of sulphuric acid and water, and of aqueous solutions of a large number of salts. In 1889 he embodied the whole in the monograph already referred to. In a paper communicated to the Transactions in 1887 (51, 779), he stated his views in the following words: "Solutions may be regarded as strictly definite atomic chemical combinations at temperatures higher than their dissociation temperatures. Definite chemical substances may be either formed or decomposed at temperatures which are higher than those at which dissociation commences; the same phenomenon occurs in solutions; at ordinary temperatures they can be either formed or decomposed." This view was retained by Mendeléeff, and appears in a footnote (p. 64) in the 7th Russian Edition (3rd English Edition) of the *Principles*, 1902, where the following passage occurs: "The conception of solutions as dissociated definite liquid chemical compounds is based on the following considerations: (1) That there exist certain undoubtedly definite crystallised chemical compounds (such as $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$, or $\text{NaCl}, 2\text{H}_2\text{O}$, or $\text{CaCl}_2, 6\text{H}_2\text{O}$, etc.), which melt on a certain rise of temperature and then form true solutions; (2) that metallic alloys in a molten condition are real solutions, but on cooling they often give entirely distinct and definite crystallised compounds; (3) that between the solvent and the substance dissolved there are formed in a number of cases many undoubtedly definite compounds, such as compounds with water of crystallisation; (4) that the physical properties of solutions, and especially their specific gravities (a property which can be very accurately determined), vary with a change in composition, and in such a manner as would be required by the formation of one or more definite but dissociating compounds. . . . The increase in specific

gravity (ds) varies in all well-known solutions with the proportion of substance dissolved (dp), and this dependence can be expressed by a formula $ds/dp = A + Bp$ between the limits of definite compounds, whose existence in solutions must be admitted." Applying this method, he concludes that mixtures of alcohol and water may contain several definite compounds, such as $C_2H_6O + 3H_2O$. These views, however, did not prevent his recognising van't Hoff's gas theory as applicable to dilute solutions.

In conjunction with some of his students, Mendeléeff also studied minutely the question of the elasticity of gases, and published several papers on the subject (see Royal Soc. Catalogue), extending over a period of some ten years from 1872. From the earlier researches of Regnault and others, it was known that the law of Boyle and Marriotte is not strictly applicable either to all gases or at all pressures. Mendeléeff and his assistants devoted special attention to the departures from the theoretical requirements of the law exhibited by gases under very greatly reduced pressures. He found that for hydrogen the value of pv diminishes with the pressure down to 20 mm., while for air, carbon dioxide, and some others, pv increases slightly to a maximum.

Another subject to which Mendeléeff gave a good deal of attention was the nature and origin of petroleum. Having already reported in 1866 on the naphtha springs in the Caucasus, in the summer of 1876 he crossed the Atlantic and surveyed the oil fields of Pennsylvania. In the course of these investigations, he was led to form a new theory of the mode of production of these natural deposits. The assumption that the oil is a product of the decomposition of organic remains he rejects on a variety of grounds, which are set forth in a communication to the Russian Chemical Society (Abstract, see *Ber.*, 1877, **10**, 229). Mendeléeff assumes, as others have done, that the interior of the earth consists largely of carbides of metals, especially iron, and that hydrocarbons result from the penetration of water into contact with these compounds, metallic oxide being formed simultaneously. The hydrocarbons are supposed to be driven in vapour from the lower strata, where temperature is high, to more superficial strata, where they condense and are retained under pressure. In 1886, in consequence of rumours as to the possible exhaustion of the Russian oil fields, he was sent by the Government to Baku to collect information, and in 1889 he made a communication on this subject to Dr. Ludwig Mond, which is printed in the *Journal of the Society of Chemical Industry* (1889, **8**, 753.)

The influence of the great generalisation known as the periodic law can best be estimated by reviewing the state of knowledge

and opinion before the announcement and acceptance of the principle by the chemical world, and subsequently glancing at the influence which, directly or indirectly, it has produced on scientific thought, not only in regard to the great problems to which it immediately relates, but to the whole range of chemical theory.

The use of the expression, "atomic weight," implies the adoption of some form of atomic theory. But forty or more years ago Dalton's atomic theory was by many of the most philosophical chemists and physicists regarded as only a convenient hypothesis, which might be temporarily useful, but could not be accepted as representing physical reality. Since that time, however, a variety of circumstances have contributed to consolidate the Daltonian doctrine. The estimation of the ratios called atomic weights has been the subject of research, attended by more and more elaborate precautions to secure accuracy, from the time of Dalton himself onward through successive generations down to the present day. Though the atomic weights of the majority of the common elements are now known to a high degree of accuracy, the acknowledged errors have been sufficiently great to render abortive various attempts to reduce them to any common scheme of mathematical relationship. As is well known, the most important step toward the systematisation of atomic weights was taken about 1860, mainly on the grounds eloquently and convincingly set forth by Cannizzaro,* in consequence of which the arbitrary selection of numbers for atomic weights was superseded by the practical recognition of the law of Avogadro and the application of the law of Dulong and Petit, so that a common standard was established. No general scheme of atomic weights was previously possible, partial and imperfect efforts in this direction being represented by Döbereiner's triads and the principle of homology made use of by Dumas. Only so soon as numbers representing the atomic weights of calcium, barium, lead, and other metals were corrected and brought into the same category as those of oxygen, sulphur, and carbon was there some chance of determining whether these numbers possessed a common factor or were capable of exhibiting mathematical interrelations which might be regarded as symbolic of physical relations or even directly dependent upon them. The first step in this direction was taken by J. A. R. Newlands, who, after some preliminary attempts in 1864-1865, discovered that when the elements are placed in the order of the numerical value of their atomic weights, corrected as advised by Cannizzaro, the eighth element starting from any point on the list exhibits a revival of the characteristics of the first. This undoubtedly repre-

* 1858, and later, Faraday Lecture, 1872.

sents the first recognition of the principle of periodicity in the series of atomic weights, but whether discouraged by the cool reception of his "law of octaves" by the chemical world or from imperfect apprehension of the importance of this discovery, Newlands failed to follow up the inquiry. It was not long, however, before the matter was taken up by others, and doubtless the improvements in the estimation of atomic weights, following on the work of Stas, then only recently published, inspired greater confidence in the approximate accuracy of the numbers adopted as atomic weights, and thus encouraged inquiry into their relations. The subject is, indeed, an attractive one, for it involves considerations which lie at the foundations of all our notions respecting the physical constitution of matter, and accordingly we find papers by many chemists dealing with the question of these numerical relations. Odling especially seems to have given much thought to the subject, and, ignoring Newlands' previous attempts, he drew up towards the end of 1864 * a table containing a list of all the then well-known elements, arranged horizontally in the order of their generally accepted groups, and perpendicularly in the order of their several atomic weights. He concludes an article in Watts's Dictionary a few months later with these words: "Doubtless some of the arithmetical relations exemplified in the foregoing table are merely accidental, but, taken altogether, they are too numerous and decided not to depend on some *hitherto unrecognised* law." It is important to note the words I have italicised.

Such, then, was the state of knowledge about this time. Evidently the way was being prepared, but the prophet had not made his appearance, the seer who could look with the eyes of confidence beyond the clouds of uncertainty which obscured all ordinary vision.

In March, 1869, Mendeléeff communicated to the Russian Chemical Society an enunciation of the principle of periodicity and a statement of some of the consequences of this recognition of the relation of properties to atomic weight throughout the whole range of the known elements, and this statement was accompanied by a table which, while it bears a close resemblance to Odling's table of 1864, was apparently connected in his mind with an idea which became clearer and more decisive in the modifications which he immediately afterwards introduced into the arrangement.†

* *Quart. J. Sci.*, 1864, 1, 643; and Watts' Dict., Vol. III, 975.

† Subjoined is a translation, as literal as possible, of the German Abstract (*Zeitsch. f. Chem.*, 5, 405). Several obvious misprints have been corrected.

On the Relation of the Properties to the Atomic Weights of the Elements.

By D. MENDELÉEFF.

When the elements are arranged in vertical columns, according to increasing atomic weight, so that the horizontal lines contain analogous elements, again according to increasing atomic weight, the following arrangement results, from which several general conclusions may be derived:

			Ti = 50	Zr = 90	? = 180
			V = 51	Nb = 94	Ta = 182
			Cr = 52	Mo = 96	W = 186
			Mn = 55	Rh = 104.4	Pt = 197.4
			Fe = 56	Ru = 104.4	Ir = 198
			Ni = Co = 59	Pd = 106.6	Os = 199
			Cu = 63.4	Ag = 108	Hg = 200
H = 1			Zn = 65.2	Cd = 112	
	Be = 9.4	Mg = 24	? = 68	U = 116	Au = 197 ?
	B = 11	Al = 27.4	? = 70	Su = 118	
	C = 12	Si = 28	As = 75	Sb = 122	Bi = 210 ?
	N = 14	P = 31	Se = 79.4	Te = 128 ?	
	O = 16	S = 32	Br = 80	I = 127	
	F = 19	Cl = 35.5	Rb = 85.4	Cs = 133	Tl = 204
Li = 7	Na = 23	K = 39	Sr = 87.6	Ba = 137	Pb = 207
		Ca = 40	Ce = 92		
		? = 45	La = 94		
		?Er = 56	Di = 95		
		?Yt = 60	Th = 118		
		?In = 75.6			

1. The elements arranged according to the magnitude of atomic weight show a periodic * change of properties.

2. Chemically analogous elements have atomic weights either in agreement (Pt, Ir, Os), or increasing by equal amounts (K, Rb, Cs).

3. The arrangement, according to atomic weights, corresponds with the *valency* of the elements, and to a certain extent the difference in chemical behaviour, for example, Li, Be, B, C, N, O, F.

4. The elements most widely distributed in nature have small atomic weights, and all such elements are distinguished by their characteristic behaviour. They are thus *typical* elements, and the lightest element, hydrogen, is therefore rightly chosen as the typical unit of mass.

5. The magnitude of the atomic weight determines the properties of the element, whence in the study of compounds regard is to be paid not only to the number and properties of the elements and their mutual action, but to the atomic weights of the elements. Hence the compounds of S and Te, Cl and I, show, beside many analogies, yet striking differences.

* Here an error in the German translation does an injustice to the original inasmuch as the Russian word for periodical is rendered "stufenweise" (gradual).

6. It allows the discovery of many *new* elements to be foreseen, for example, analogues of Si and Al with atomic weights between 65 and 75.

7. Some atomic weights will presumably experience a correction; for example, Te cannot have the atomic weight 128, but 123 to 126.

8. From the foregoing table, new analogies between elements become apparent. Thus U appears as an analogue of B and Al, which, as is well known, has long ago been established experimentally.

Previous students of the subject had been, for the most part, struck with the relations obviously subsisting between the members of the several natural families of elements, but had, with few exceptions, failed to perceive that there must be a *general* law binding the whole together. However, Mendeléeff, with that noble sentiment of justice which always animates the truly scientific mind, admits that the idea of a general law had already been foreshadowed by others, and he says (Faraday Lecture, 1889), "I now see clearly that Strecker, de Chancourtois, and Newlands stood foremost in the way towards the discovery of the periodic law, and that they merely wanted the boldness necessary to place the whole question at such a height that its reflection on the facts could be clearly seen."

It may be remarked that Strecker did little more than call attention to the sequence in the values of the atomic weights of certain elements, and states that "we must leave to the future the discovery of the *law* of the relations which appear in these figures" (Theorien u. Experimente zur Bestimmung der Atomgewichte der Elemente, 1859). De Chancourtois, in his work entitled "Le Vis Tellurique" (1863), devised a geometric method of representing the atomic weights by coiling round a cylinder a helix with an angle of 45° , the cylinder being divided vertically into sixteen equal parts by lines drawn from the circular base. The points of intersection of the helix with these lines were supposed to represent the atomic weights of elements which differed from one another by 16 or by multiples of 16.

Mendeléeff's table of 1869 was subsequently in 1871 modified so as to assume the form with which we have all been so long familiar, and which is to be found in every modern text-book. Thus it may be claimed for Mendeléeff that he was actually the first, not only to formulate a general law connecting atomic weights with properties, but was the first to indicate its character, and, as himself (*Principles*, 1905, II, p. 28) has pointed out, he was the first "to foretell the *properties of undiscovered* elements, or

ter the accepted atomic weights" in confidence of its validity. time was, in fact, ripe for the enunciation of this general ciple, and, the suggestion once given, the relations embodied in the law could not fail to attract other chemists. Accordingly, in December, 1869, Lothar Meyer, with such knowledge of Mendeléeff's scheme as could be derived from the imperfect German translation of his paper of the previous March, proved himself an independent exponent of the idea by contributing to Liebig's *Annalen* a paper containing a table, substantially identical with that of Mendeléeff, and his famous diagram of atomic volumes, which, more clearly even than the tabular scheme, illustrates the principle of periodicity.

The history of science shows many instances of the same kind. Most generalisations have often resulted from the gradual accumulation of facts which, after remaining for a time isolated and confused, have been found to admit of co-ordination into a comprehensive scheme, and, this once clearly formulated, many workers are found ready to assist in its development. The case is an early parallel to the recognition of the operation of natural selection by Darwin and Wallace, or it might be compared to the discovery of oxygen by Priestley and Scheele and the utilisation of his knowledge by Lavoisier. In each case much preparatory work had been done, and a body of knowledge had been gradually accumulated which, when duly marshalled and surveyed by the eye of a master, could scarcely fail to reveal to him the underlying principle. The full consequences, however, would appear only to time.

The law of periodicity was expressed by Mendeléeff in the following words: *

The properties of the elements, as well as the forms and properties of their compounds, are in periodic dependence on, or, expressing ourselves algebraically) form a periodic function of, the atomic weights of the elements." After a brief historical introduction of the discovery of the law by himself, Mendeléeff concludes by saying (*Principles*, p. 18): "I consider it well to observe that no law of nature, however general, has ever been established all at once; its recognition has always been preceded by many presentiments; the establishment of a law, however, does not take place when the first thought of it takes place, or even when its significance is recognised, but only when it has been confirmed by the results of experiment which the man of science must consider as the only proof of the correctness of his conjectures and opinions."

* *Principles*, 1905, Vol. II, p. 17.

I regard it as unnecessary, in the presence of the Fellows of the Chemical Society, to review with any detail the multitudinous applications of the scheme of the elements constructed on the basis of the periodic law. These are the commonplaces of modern theoretical chemistry. They are embodied in every text-book of any importance, and are related by every lecturer and teacher as familiar and indisputably recognised consequences of the system. We may therefore pass lightly over the story of the prediction by Mendeléeff of the properties of undiscovered elements, confirmed so remarkably by the discovery of scandium, gallium, and germanium, and related in dramatic language by Mendeléeff himself (Faraday Lecture). We may also pass over the applications of the system to the correction of atomic weights, illustrated by the case of beryllium, the recognition of previously unnoticed relations, and the discovery of new elements, notably the companions of argon (Ramsay, Presidential Address to Section B, British Association, 1897, and *Proc. Roy. Soc.*, 1898, 63, 437).

It will be more profitable to consider a few of the difficulties which still encumber the application of the law, and which, while limiting our acceptance of it in an unqualified form as applicable to the whole of the elements, tempt the speculative mind to wander in wide fields of conjecture.

Can it be truly said that the elements arranged in the order of their atomic weights show without exception periodic changes of properties? This question has been propounded already, but has never been fully discussed, even by Mendeléeff. An examination of the facts seems, however, to indicate the possibility of some other principle, which, while it does not supersede the periodic scheme, would, if it could be recognised, supplement it. This involves other considerations which we may turn to first.

If the whole of the known elements are drawn up in the order of their atomic weights (using the values given by the International Committee for 1908), we find a progression in value from $H=1.008$ to $U=238.5$, with differences between the successive elements which vary from 0.3 (Co-Ni)* to 4.3 (Co-Cu) among the

* Mendeléeff held the view that "in general, cobalt is more nearly allied to iron than nickel, and the latter more nearly to copper" (*Principles*, Eng. Ed., 1905, p. 37^a). Accordingly, in the first edition of his book, he assigned to cobalt the atomic weight 58.5, and to nickel, the atomic weight 59. In the later edition of 1905, he makes them both 59, and expresses the belief that eventually the atomic weight of cobalt will be found less than that now accepted and less than nickel (Eng. Ed., 1905, II, footnote 25, p. 45). Whatever may be the exact values of the atomic weights of these two elements, there can be no doubt that the atomic weight of cobalt is *greater* than that of nickel. This is proved by the estimations of the specific heats of both these metals purified by methods which preclude the possibility

common elements of which the atomic weights have been most accurately estimated. The large difference, 7·4, between Sb and Te is manifestly due to some error in the atomic weight of tellurium of which no sufficient explanation is yet forthcoming, and it is only when we get to the element Bi that there seems reason for thinking that it must be followed by some hitherto unrecognised elements, since the gap between Bi and the next known element, Ra, is 18·7 units. The atomic weights of the long series of elements beginning with La are confessedly uncertain, but that they all lie between La and Ta seems probable, because although the individual numbers are doubtless inexact, the *average* difference between any two consecutive terms is roughly the same as the average difference between successive atomic weights among the better known elements preceding them. $Ta - La = 181 - 138·9 = 42·1$ for sixteen intervals.

It must also be noted that the differences, approximately three units each, among the three elements with smallest known atomic weights, namely,

H 1·008, He 4, Li 7·03,

are greater than the differences observed among the elements which immediately succeed them, namely,

Li 7·03, Be 9·1, B 11, C 12, N 14·01, O 16, F 19.

It will be seen later that, as regards this part of the scheme, Mendeléeff had put forth a special hypothesis.

If these considerations are to be regarded as having weight, it seems probable that few additional elements are to be expected, except possibly one following Mo and another following W, save in the region already indicated from Bi to Ra. This suggests the remark that, after all, it is not necessary to assume that the materials of which the earth consists should necessarily include a sample of every possible element indicated by such a scheme. Some which are missing from terrestrial matters may perhaps be responsible for phenomena recognisable by the spectroscope in stars or nebulae far distant in cosmical space. The unexpected, however, often happens, and, remembering the discovery of terrestrial of appreciable error or of mutual contamination. The following results were obtained by different observers using different methods:

Temperature.	Cobalt.	Nickel.
From 100° to 15°	0·10303	0·10842
„ 15° to -78·4°	0·0939	0·0975
„ 78·4° to -182·5°	0·0712	0·0719

Tilden, *Phil. Trans.*, 1900, **194 A**, 249.

From 100° to 20°	0·104	0·108
-------------------------------	-------	-------

Copaux, *Compt. rend.*, 1905, **140**, 657.

helium, it is permissible to hope that some of the vacant spaces may hereafter be filled by earthly occupants.

There is one important point to be noted here, namely, that if the so-called rare earth metals, praseodymium, neodymium, samarium, gadolinium, terbium, dysprosium, erbium, ytterbium, and others of which the existence is doubtful, do lie in the position indicated, the original statement of the periodic law breaks down at this point. Enough is already known of their properties to show that they are very closely allied together, and cannot fall into separate periods. Mendeléeff says (*Principles*, 1905, Vol. II, p. 45), "This appears to me to be one of the most difficult problems offered to the periodic law." He prefers, however, to leave open the question as to the position of these elements. The discordance of argon and of tellurium with the places assigned to them are also matters which must be left for the consideration of future workers.

One result of the recognition of the periodic law is that theories concerning the genesis of the elements have received a stimulus previously unknown. It is, however, interesting to note the attitude of Mendeléeff toward this question, and the small extent to which this attitude appears to have become modified with the lapse of time. When, in 1889, twenty years after the discovery of the law, he composed the Faraday lecture, he seems to have regarded speculation in this direction as a kind of abuse of the periodic system. He was, of course, fully justified in stating (Faraday Lecture) that "the periodic law, based as it is on the solid and wholesome ground of experimental research, has been evolved independently of any conception as to the nature of the elements; it does not in the least originate in the idea of a unique matter; and it has no historical connexion with that relic of the torments of classical thought." But it is at least questionable how far he was justified in continuing that "therefore it affords no more indication of the unity of matter, or of the compound character of our elements, than the law of Avogadro or the law of specific heats, or even the conclusions of spectrum analysis. None of the advocates of a unique matter have ever tried to explain the law from the standpoint of ideas taken from a remote antiquity, when it was found convenient to admit the existence of many gods and a unique matter." And again, later, "From the foregoing, as well as from the failures of so many attempts at finding in experiment and speculation a proof of the compound character of the elements and of the existence of primordial matter, it is evident, in my opinion, that this theory must be classed among mere utopias."

Fifteen years later, after the discovery of the argon group of elements, of the phenomena of radioactivity, and of radium, it became necessary to consider the relations of these substances to the periodic scheme. In a remarkable article contributed to the new Russian Encyclopædia, and subsequently printed as Appendix III to the *Principles* (English Edition, 1905), Mendeléeff gives a new table of the elements, in which places are found, not only for the argon group and radium, but for two hypothetical elements which are placed before helium and designated x and y .

As this table may be assumed to represent his latest views concerning the relations of the elements, it is here reproduced.*

The y in the table is supposed to be an analogue of helium, and may be identified hereafter with "coronium," which has been recognised in the sun's coronal atmosphere. This gas would have, according to Mendeléeff, a density about 0.2, and therefore a molecular weight about 0.4, or about one-tenth that of helium.

x is the "ether" of the physicist, for which Mendeléeff, disregarding conventional views, supposes a molecular structure. He also assumes that, like the argon group, this element is chemically inert and possesses a very low density and atomic weight, estimated at 0.000,000,000,053.

His views in connexion with this matter are put forward merely as speculations and without dogmatism, but it is clear that he retained his repugnance to the conception of a unique matter to the last. In his essay entitled "A Chemical Conception of the Ether" (translated by Kamensky, 1904), the following passage occurs, p. 32: "Being unable to conceive the formation of the known elements from hydrogen, I can neither regard them as being formed from the element x , although it is the lightest of all the elements. I cannot admit this, not only because no fact points to the possibility of the transformation of one element into another, but chiefly because I do not see that such an admission would in any way facilitate or simplify our understanding of the substances and phenomena of nature."

Chemists and physicists have, however, found it impossible to resist the fascination of this problem, and accordingly there have been many hypotheses as to the origin of the elements and the nature of their connexion with one another. These seem to be inseparable from the periodic scheme itself, which at once provokes the inquiry, Why do these numerical relations occur, and what

* The spaces left vacant in Series I, after hydrogen, are the positions of hypothetical elements having approximately the atomic weights, 1.4, 1.3, 2.2, 2.6, 2.8, 3.0, and 3.4, and standing at the head of groups II to VIII respectively.

Series.	Zero group.	Group I	Group II.	Group III.	Group IV.	Group V.	Group VI.	Group VII.	Group VIII.
0 ...	<i>x</i>	—	—	—	—	—	—	—	—
1 ...	<i>y</i>	Hydrogen, H = 1.008	—	—	—	—	—	—	—
2 ...	Helium, He = 4.0	Lithium, Li = 7.03	Beryllium, Be = 9.1	Boron, B = 11.0	Carbon, C = 12.0	Nitrogen, N = 14.04	Oxygen, O = 16.0	Fluorine, F = 19.0	—
3 ...	Neon, Ne = 19.9	Sodium, Na = 23.05	Magnesium, Mg = 24.1	Aluminium, Al = 27.0	Silicon, Si = 28.4	Phosphorus, P = 31.0	Sulphur, S = 32.06	Chlorine, Cl = 35.45	—
4 ...	Argon, Ar = 38	Potassium, K = 39.1	Calcium, Ca = 40.1	Scandium, Sc = 44.1	Titanium, Ti = 48.1	Vanadium, V = 51.4	Chromium, Cr = 52.1	Manganese, Mn = 55.0	Iron, Fe = 55.9
5 ...	—	Copper, Cu = 63.6	Zinc, Zn = 65.4	Gallium, Ga = 70.0	Germanium, Ge = 72.3	Arsenic, As = 75.0	Selenium, Se = 79.0	Bromine, Br = 79.95	Cobalt, Co = 59
6 ...	Krypton, Kr = 81.8	Rubidium, Rb = 85.4	Strontium, Sr = 87.6	Yttrium, Y = 89.0	Zirconium, Zr = 90.6	Niobium, Nb = 94.0	Molybdenum, Mo = 96.0	—	Nickel, Ni = 59 (Cu)
7 ...	—	Silver, Ag = 107.9	Cadmium, Cd = 112.4	Indium, In = 114.0	Tin, Sn = 119.0	Antimony, Sb = 120.0	Tellurium, Te = 127	Iodine, I = 127	—
8 ...	Xenon, Xe = 128	Cesium, Cs = 132.9	Barium, Ba = 137.4	Lanthanum, La = 139	Cerium, Ce = 140	—	—	—	—
9 ...	—	—	—	—	—	—	—	—	—
10 ...	—	—	—	Ytterbium, Yb = 173	—	Tantalum, Ta = 183.0	Tungsten, W = 184	—	—
11 ...	—	Gold, Au = 197.2	Mercury, Hg = 200.0	Thallium, Tl = 204.1	Lead, Pb = 206.9	Bismuth, Bi = 208	—	—	Osmium, Os = 191
12 ...	—	—	Radium, Rd = 224	—	Thorium, Th = 232	—	Uranium, U = 239	—	Iridium, Ir = 193
									Platinum, Pt = 194.9 (Au)

is the meaning of them if they do not point to a common genesis or the operation of some process of evolution?

Hypotheses concerning the evolution of the elements have hitherto been usually based on the assumption that the successive stages of condensation of elemental matter proceeded from a single primary stuff, which by a process analogous to polymerisation among carbon compounds gave rise to atoms of greater and greater mass, which were stable at the prevailing and any lower temperature. The physical cause of the successive condensations is supposed to be a falling temperature. It is, of course, possible to imagine that if to the stuff of which hydrogen atoms consist are added successive portions of matter of the same kind, stable structures may at intervals result which we know as the atoms of the elements helium, lithium, beryllium, boron, carbon, nitrogen, oxygen, and fluorine, provided the idea of internal structure in these atoms is allowed. Otherwise, from the mere accretion of matter upon a central nucleus, there seems no sufficient reason why there should not have been formed an indefinite number of intermediate masses corresponding to an indefinite number of what would be called elements. Further, it is difficult to understand why simple increase of mass should change, say, oxygen into fluorine, while a further addition of the same kind should change negative fluorine into inert neon or positive sodium. The possibility of the condensation of a single "protyl" so as to produce, at successive though unequal stages of cooling, the elements known to the chemist has been most ably discussed long ago by Sir William Crookes.

This hypothesis, however, was put forward long before the work of Sir J. J. Thomson and his school was given to the world and the electron was accepted as a physical reality. The hypothesis that one elemental stuff may give rise to the whole array of known elements by a process of condensation accompanied by a loss or gain of electrons, the mass of which is approximately one-thousandth of the mass of an atom of hydrogen, forms the subject of a paper by Mr. A. C. G. Egerton in a recent number of our Transactions (1909, 95, 239). The atomic weights calculated by his formula agree closely with the experimental atomic weights of the first fifteen elements, but the hypothesis gives no explanation of the facts observed in the physical properties of the elements arranged according to the Mendeléeff scheme, their alternation of odd and even valency, the transition from positive on one side of the table to negative on the other, the periodicity of properties shown by the sudden change of character in passing from fluorine to the next element, whether it be neon or sodium.

Another paper by Messrs. A. C. and A. E. Jessup (*Phil. Mag.*,

1908, [vi], 15, 21) has recently provided a hypothesis of an entirely different character. From a study of the spectra of the nebulae, these authors have been led to assume the existence of two hitherto unrecognised elements, to which the names protoglucinum and protoboron are assigned. These with hydrogen and helium are supposed to represent *four* initial substances, or protons, which, by condensation directly or indirectly, give rise to all the rest of the elements. The arguments of these authors are ingenious, but rather artificial in view of the fact that the number of groups in the periodic scheme to be provided for is greater than four.

In the Mendeléeff chart of the elements, there is nothing more striking than the gathering of the negative elements toward what may be called the N.E., and the segregation of the positive elements toward the S.W., the centre of the intermediate territory being occupied by elements which play a more or less undecided part. I have elsewhere (Presidential Address, 1905, Trans., 87, 564) drawn attention to the fact that carbon, at any rate, is not directly deposited by electrolysis from any of its compounds, with positive hydrogen on the one hand, or negative chlorine on the other. I believe the same is true of silicon, these two elements standing in a middle position between the extremes occupied by lithium and fluorine respectively.

If we assume that atoms are made up of two parts (protyls), positive and negative, in proportions which determine by the preponderance of one or the other whether the element shall exhibit the positive character of a metal like lithium or the negative character of a halogen, we arrive at a hypothesis which recalls the ideas put forward nearly a century ago by Berzelius. His views are familiar to every student of the history of chemistry, but have long been relegated to the lumber room of worn-out doctrine. The last few years have, however, given us the remarkable experimental investigations of J. J. Thomson already referred to, and the new conceptions concerning the nature of atoms, which revive the fundamental idea that they are made up of two components.*

* Carnelley, in 1885 (*Brit. Assoc. Reports*), brought forward the idea "that the elements are not elements in the strict sense of the term, but are, in fact, compound radicals made up of at least two simple elements, A and B." The element A was supposed to be identical with carbon, while to B was assigned a negative weight, -2, and it was suggested that it might be the ether of space. C. S. Palmer (*Proc. Colorado Scient. Soc.*) assumed the existence of two sub-elements, to which he gave the names "kalidium" and "oxidium," and his views appear to have a general resemblance to the hypothesis suggested in the text. The original article is abstracted in Venables' *Periodic Law* and is referred to in footnotes in Palmer's translation of *Nernst's Theoretical Chemistry*.

Setting out the known elements in the order of the numerical value of their atomic weights, we find that between the first three elements, $H=1$, $He=4$, and $Li=7$, the difference, 3, is greater than would be expected by comparison with the differences noticed between the elements of greater atomic weight which immediately follow them. In order to satisfy the hypothesis just put forward, there appears to be wanting an element which should stand in the same relation to fluorine as hydrogen to lithium. This would have an atomic weight 2.7 approximately. Whether this exists, and whether its existence is indicated by the unappropriated spectral lines of nebulae or corona, can only be a matter of conjecture. Mendeléeff, in his (1905) latest speculations concerning the possibility of still undiscovered elements, has suggested the existence of a new element of the halogen group with an atomic weight about 3.* But, as already sufficiently shown, he accepted no hypothesis which involved any idea of the composite nature of the elements. It would therefore have been foreign to his system to employ this element in any such manner. But the idea seems to me to assist materially conceptions as to the process of condensation hypothetically occurring in the evolution of the known chemical elements. For to suppose that the typical elements, so different as they are in character, forming the first line of Mendeléeff's scheme, have all resulted from the condensation of a single protyl has always seemed to me a difficult proposition. There is comparatively little difficulty in the view that the successive terms of a family of what, by analogy, may be called a homologous series, may have originated in this way. A consideration of all the properties of the alkali metals, for example, coupled with the character of their spectra, suggests quite naturally the passage from lithium to sodium, and so forth, step by step, by the addition of successive accretions of the same matter to the primal element, the character of which, including valency, is not only sustained through the whole family, but becomes more strongly marked in proportion to the gradual increase of atomic weight. At the opposite end of the table, on the other hand, a *reduction* of the negative character of the element, in passing from fluorine to iodine, seems to suggest that the negative protyl which preponderates in the smaller atom is modified in the larger atom by the addition of a certain proportion of the positive protyl.

The conceptions presented to us in J. J. Thomson's work permit of several supplementary hypotheses, especially the idea that if

* It may also, perhaps, be worthy of note that Mr. Egerton's calculations (*loc. cit.*) lead him to postulate an element of nearly this atomic weight, namely, 2.9344, although his paper gives no indication as to its character.

atoms are really made up of smaller corpuscles these are not thrown together in confusion but, as he has shown, must be distributed within the mass in a definite order, which is determined by the attraction of the electro-positive shell and the self-repulsion of the negative corpuscles included in it. Once the idea of structure within the atom is admitted, the possibility presents itself of there being for the same mass more than one arrangement corresponding to what is called isomerism in compounds. In this way the case of elements with similar properties and identical or nearly identical atomic weights, for example, cobalt and nickel, and even such a case as tellurium, might perhaps be explained. Further, now that the materials which have so long received the unsatisfactory designation of the "rare earths" are found in unexpected abundance, it may be hoped that the study of their chemical characters may be completed. It may turn out that this group may include elements of identical atomic weight, though exhibiting different properties. It does not seem very long ago in the memory of many now living that the nature of the isomerism of the derivatives of benzene was a deep mystery, from which nearly all obscurity cleared away in the light of the then new theory of the constitution of benzene.

I have dwelt at some length on these various hypotheses, because the discussion of the subject to which they relate indicates, in my opinion, one of the consequences of the promulgation and general acceptance of the periodic scheme of the elements. This is, however, not the only result of the recognition of its validity and usefulness by chemists generally. That the elements stand in a definite relation to one another implies that their compounds also fall into their places in an orderly system, and consequently a basis is provided for the complete systematisation of the whole science of chemistry. There is scarcely a treatise on chemistry which does not bear evident witness to this influence. And this is perhaps not the least among the services rendered by this generalisation, for not only is the learner enabled to remember a much larger number of facts than previously, but he is led to perceive a connexion between phenomena and processes which was almost entirely wanting so long as practical chemistry consisted mainly of a bundle of recipes. And here it is fitting that we should glance at the famous treatise by Mendeléeff himself, "The Principles of Chemistry," of which we possess three editions in English, the last of which, issued in 1905, is a rendering of the seventh edition (1903) of the original. An eighth Russian edition began to be issued in 1905, but is incomplete. To this remarkable book it is impossible to do justice in a brief notice or to communicate to

those who have not read it an adequate impression. Clearly it is a work of genius, but such works are not always the most suitable for beginners, though for the advanced student nothing can be more inspiring. The "Principles" embody in reality two distinct treatises, for the text, which is written in an easy style, open to quite straightforward reading, is accompanied by notes which are often more voluminous and usurp entire pages. Even the preface is attended by these commentaries, which are all interesting as showing the spirit of the writer and the restless activity of his mind. A few extracts from the preface will serve to illustrate the truism too often neglected by writers of biographies, that it is impossible to separate a man's work from his life, and that the character and quality of the former are dependent upon the personal characteristics of the man, independently of the opportunities or influences which may have served to assist or to repress his activities.

"If statements of fact," he says, "themselves depend upon the persons who observe them, how much more distinct is the reflection of the personality of him who gives an account of methods and philosophical speculations forming the essence of a science! For this reason there will inevitably be much that is subjective—bearing the stamp of time and locality—in every objective exposition of science. And as an individual production is only significant in virtue of that which has preceded it and that which is contemporary with it, it resembles a mirror, which in reflecting exaggerates the size and clearness of neighbouring objects, and causes a person near it to see reflected most plainly those objects which are on the side to which it is directed, and sometimes even the person holding the mirror. Although I have endeavoured to make my book a true mirror directed toward the whole domain of chemical changes and of the elements taking part in them, yet involuntarily those influences near to me being most clearly reflected and the most brightly illuminated have tinted the entire work with their colouring. In this way the chief peculiarity of the book has been determined. Experimental and practical data and their application in life and industry occupy their place, but the philosophical principles of our science form the chief theme of the work."

Later on he says, "The thought that this book might fall not only into the hands of the beginner for whom it is intended, but also of authorities who might wish to know the views held by an old disciple of science on the current problems of chemistry, greatly complicated the preparation of a new edition, for it necessitated making a selection of the most essential of the vast number of

new researches published year by year and explaining my views on them without greatly enlarging the bulk of the work. After having closely followed all the chief conquests of chemical science since the days of Berzelius, Liebig, Dumas, and Gerhardt, and having seen the triumph of much that lay neglected, and the fall of much that was exalted, I involuntarily acquired a tendency to analyse new facts, and a desire to transmit to my readers the results of such analysis, if it could, in my opinion, help towards a proper explanation and generalisation of the chemical elements. In carefully preparing this edition, I have not lost sight of the fact that I am hardly likely to publish another, and I have therefore in many cases spoken more definitely than formerly. After having been an insignificant but zealous worker in chemistry for almost half a century, I wished my book should retain some traces of how a confirmed disciple of Gerhardt regards the fundamental problems of the theory of the chemical elements at the beginning of the twentieth century. As an example, I may mention that the more I have thought on the nature of the chemical elements, the more decidedly have I turned away from the classical notion of a primary matter, and from the hope of attaining the desired end by a study of electrical and optical phenomena, and the more clearly have I recognised that first and foremost are needed truer conceptions of 'mass' and 'ether' than those in vogue at the present time. The return to electro-chemistry which is so evident in the supporters of the hypothesis of 'electrolytic dissociation,' and the notion of a splitting up of atoms into 'electrons,' in my opinion only complicate, and in no way explain, so real a matter (since the days of Lavoisier) as the chemical changes of substances, which led to the recognition of the invariable and ponderable atoms of simple bodies. The definition of mass gave a means for analysing and grasping chemical transformation of substances, and for arriving at the atom, while the mass of the atom was shown by the periodic law to influence all its chief chemical properties. Thus chemistry in its principles stood on the firm foundations laid by Galileo, Newton, and Lavoisier, and in order to gain further insight and knowledge of the atoms themselves, the fundamental conceptions of mass, gravity, and ether will have to be explained by a method of experiment alone, otherwise the realism of science will again open its doors to such metaphysical and 'metachemical' conceptions as phlogiston and other mystical dreams. For my part I endeavour to remain true to the testament of realism left by Newton and Lavoisier, and it is my wish to instil this sentiment into my young readers."

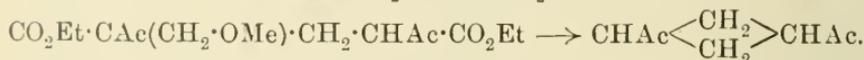
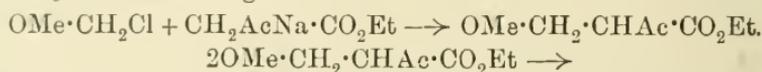
This is very clear, and little more remains to be said. In the seventeenth century Robert Boyle taught us how to distinguish elements from compounds, and how to give to the word "element" a definite connotation clearly distinguishing it from the elusive and fantastic language of the alchemists. In the eighteenth century Lavoisier showed the true nature of the most familiar of chemical compounds, namely, acids, bases, and salts, and helped to lay the foundation of quantitative chemistry. At the beginning of the nineteenth century Dalton gave to chemistry the Atomic Theory, of which it is not too much to say that it provided the scaffold by the aid of which the entire fabric of modern theoretical chemistry has been built up. Sixty years later this conception, developed and adorned by the labours of an army of earnest workers, has been shown to us in a brilliant new light thrown over the whole theory by Mendeléeff.

The views of Boyle, of Lavoisier, and of Dalton have been corrected by experience and broadened by extended knowledge, but the fundamental and essential parts of their ideas remain, and their names are immortal. In like manner the expression of the periodic law of the elements as known to the present generation is destined, we may believe, to be absorbed into a more comprehensive scheme by which obscurities and anomalies will be cleared away, the true relations of all the elements to one another revealed, and doubts as to the doctrine of evolution resolved in one sense or the other. But as with the Atomic Theory itself, there is no reason to doubt that the essential features of the periodic scheme will be clearly distinguished through all time, and in association with it the name of Mendeléeff will be for ever preserved among the Fathers or Founders of Chemistry.

CCXXVI.—*Syntheses with the Aid of Monochloromethyl Ether. Part II. The Action of Monochloromethyl Ether on the Sodium Derivative of Ethyl Acetoacetate.*

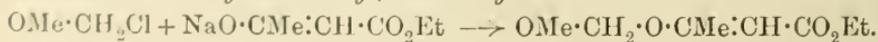
By JOHN LIONEL SIMONSEN and ROBERT STOREY.

IN a recent communication (Trans., 1908, **93**, 1777) it was shown that monochloromethyl ether readily condenses with ethyl sodio-malonate, with the formation of ethyl β -methoxymethylmalonate, and, since this substance exhibited rather striking properties, it seemed a matter of some interest to investigate also the condensation of monochloromethyl ether and ethyl sodioacetoacetate. It seemed probable that this reaction would lead to ethyl β -methoxymethylacetoacetate, which it was hoped might, on hydrolysis with acids, undergo internal condensation with formation of 1:3-di-acetylcyclobutane, and thus throw further light on the stability of the cyclobutane ring:



On carrying out the condensation in a manner similar to that described in the previous communication, besides a substance of high boiling point, an ester was isolated which was apparently the expected substance, ethyl β -methoxymethylacetoacetate. Considerable difficulties were, however, at first encountered in attempting to examine the properties of this ester, owing to the ease with which it is decomposed into acetone and formaldehyde. Satisfactory results were, however, ultimately obtained on hydrolysis with aqueous potassium hydroxide, when a beautifully crystalline acid, $\text{C}_6\text{H}_{10}\text{O}_4$, which melted at 105° , was obtained. Owing to the great stability exhibited by this acid, it was, however, at once obvious that it could not be a monosubstituted derivative of acetoacetic acid.

Now Claisen (*Ber.*, 1892, **25**, 1768) has shown that ethyl chloro-carbonate and ethyl sodioacetoacetate condense with the formation of ethyl carboxyethylacetoacetate, and it therefore seemed probable that a similar reaction had taken place in this case with the formation of *ethyl methoxy- β -methoxycrotonate*:

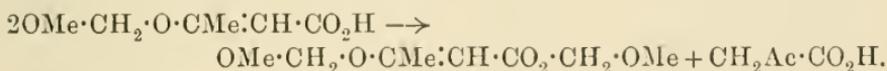


Further investigation confirmed this view, and it was found that

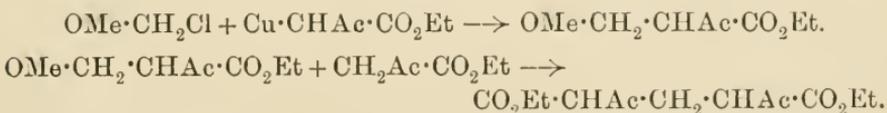
the acid $C_6H_{10}O_4$ showed in every way the properties of a substituted crotonic acid. *Methoxy- β -methoxycrotonic acid* is an acid of considerable stability; it is readily distilled under diminished pressure, and its potassium salt may be heated to 100° without any decomposition taking place. When, however, it is treated with dilute acids or heated with water in a sealed tube, it undergoes complete disintegration, with formation of formaldehyde, acetone, and carbon dioxide.

In order to obtain a still more definite proof of its constitution, an attempt was made to oxidise it with ozone in a manner analogous to that which Harries (*Annalen*, 1905, **343**, 352) employed so successfully in the case of crotonic acid. Unfortunately, however, although a solid ozonide was obtained, no satisfactory product could be isolated on decomposition with water, and only the presence of acetic acid and an aldehyde, probably formaldehyde, could be definitely proved.

Methoxy- β -methoxycrotonic acid undergoes an interesting decomposition when distilled under the ordinary pressure, two molecules reacting with the formation of a substance which is probably *methoxymethyl methoxy- β -methoxycrotonate*, the reaction taking place in accordance with the following scheme:



In continuation of these experiments, many attempts were made to produce a substance in which the monochloromethyl ether radicle is attached to the carbon atom. It has been shown by Nef (*Annalen*, 1893, **276**, 200) that ethyl chlorocarbonate readily condenses with the copper derivative of ethyl acetoacetate with the formation of ethyl acetylmalonate, and an attempt was therefore made to obtain ethyl β -methoxymethylacetoacetate in a similar manner. In this, however, we were unsuccessful, the sole product of the condensation being ethyl $\alpha\gamma$ -diacetylglutarate. It is not difficult to account for the formation of this substance if it be assumed that the process proceeds on the following lines. Ethyl β -methoxymethylacetoacetate is first formed, and this removes the copper from a portion of the copper derivative of ethyl acetoacetate, and the ethyl acetoacetate thus liberated combines with the ethyl β -methoxymethylacetoacetate with loss of methyl alcohol and formation of ethyl $\alpha\gamma$ -diacetylglutarate:



From this experiment it seems improbable that ethyl β -methoxy-

methylacetoacetate is capable of existence in the presence of ethyl acetoacetate, immediate condensation taking place.

Ethyl $\alpha\gamma$ -diacetylglutarate has already been investigated by Knoevenagel (*Annalen*, 1894, **281**, 94), who obtained it by the condensation of ethyl acetoacetate and formaldehyde in the presence of piperidine and other secondary bases. He does not, however, seem to have been able to prepare it in a pure state, since he says that it decomposes when distilled even under diminished pressure. We have found that this is not the case. It has been mentioned above (p. 2106) that an oil of high boiling point was obtained in the condensation of ethyl sodioacetoacetate and monochloromethyl ether, and this consists entirely of Knoevenagel's ethyl $\alpha\gamma$ -diacetylglutarate, which we have succeeded in obtaining quite pure by repeated distillation. Its identity was confirmed by the fact that on hydrolysis with dilute sulphuric acid it was converted into 1-methyl- Δ^1 -cyclohexen-3-one, and when treated with alcoholic ammonia it gave ethyl dihydrolutidinedicarboxylate.

It is a matter of some interest that ethyl dihydrolutidinedicarboxylate is also formed when pure ethyl methoxy- β -methoxy-crotonate is treated with alcoholic ammonia. In this case, the ammonia must first hydrolyse the ethyl methoxy- β -methoxy-crotonate with the formation of formaldehyde and ethyl acetoacetate, which then recombine in the presence of the base with separation of ethyl $\alpha\gamma$ -diacetylglutarate, and this reacts in the ordinary manner with the ammonia.

EXPERIMENTAL.

Condensation of Monochloromethyl Ether and Ethyl Sodioacetoacetate.

Finely-divided sodium (14 grams) was suspended in dry ether (350 c.c.), and ethyl acetoacetate (81 grams) was gradually added. When the vigorous reaction which takes place had completely subsided (about two hours), monochloromethyl ether (50 grams), dissolved in an equal volume of dry ether, was slowly added, and the reaction mixture well shaken and cooled. The sodium compound rapidly dissolved, and in about five minutes a gelatinous precipitate of salt separated. The next day water was added and the ether separated, dried, and evaporated. The residual oil, which, as is usually the case in condensations with monochloromethyl ether, had a strong odour of formaldehyde, was rapidly fractionated under 14 mm. pressure.

After a small quantity of unchanged ethyl acetoacetate had passed over (5 grams), the thermometer rapidly rose, and a large

fraction distilled fairly constantly at 115—125°. As soon as the temperature again began to rise, the distillation was stopped, and the residue in the flask (36 grams) was reserved for later investigation (see p. 2111).

The main fraction, boiling at 115—125°, was refractionated several times, when it was found to distil at 109—110°/18 mm. Yield, 40 grams:

0.1316 gave 0.2674 CO₂ and 0.0951 H₂O. C=55.4; H=8.0.

C₈H₁₄O₄ requires C=55.1; H=8.0 per cent.

Ethyl methoxy-β-methoxycrotonate is a colourless oil possessing a slightly pungent odour. A solution of the ester in chloroform rapidly absorbs bromine, with slow evolution of hydrogen bromide.

Methoxy-β-methoxycrotonic Acid, OMe·CH₂·O·CMe·CH·CO₂H.

Ethyl methoxy-β-methoxycrotonate (5 grams) was mixed with potassium hydroxide (5 grams) dissolved in water (25 c.c.), and heated on the boiling-water bath for four hours, when all the oil had passed into solution. After cooling, the aqueous solution was made faintly acid with hydrochloric acid, when a pale yellow solid separated.* This was collected, drained on porous porcelain, and purified by crystallisation from either ether or light petroleum:

0.1282 gave 0.2319 CO₂ and 0.0815 H₂O. C=49.3; H=7.1.

C₆H₁₀O₄ requires C=49.3; H=6.9 per cent.

Methoxy-β-methoxycrotonic acid separates from ether or light petroleum in large, glistening, prismatic needles, which melt at 105°. It is readily soluble in ether, ethyl acetate, chloroform, or boiling light petroleum, but only sparingly so in benzene. Its sodium carbonate solution immediately decolorises a solution of potassium permanganate.

When a solution of the acid in chloroform is treated with a chloroform solution of bromine, the bromine is rapidly absorbed, but in a short time hydrogen bromide is evolved, so that it was found impossible to isolate the bromo-acid.

The *silver* salt separates from a faintly alkaline solution of the ammonium salt in glistening needles, which are readily soluble in hot water. A recrystallised specimen, dried at 100°, gave the following results on analysis:

0.1776 gave 0.1887 CO₂, 0.0579 H₂O, and 0.0757 Ag. C=28.9;
H=3.6; Ag=42.6.

0.1213 gave 0.0515 Ag. Ag=42.5.

C₆H₉O₄Ag requires C=28.4; H=3.6; Ag=42.7 per cent.

* A further quantity of this acid may be obtained by extracting the filtrate with ether.

Since methoxy- β -methoxycrotonic acid should exist in *cis*- and *trans*-forms, careful search was made with the view of isolating the other form of this acid. The porous tiles on which the crude acid had been drained were extracted in a Soxhlet apparatus with ether, when an oily acid was obtained which could not be obtained crystalline. It seems possible that this oil contained a mixture of the stereoisomerides, since on distillation it gave a good yield of methoxymethyl methoxy- β -methoxycrotonate (see below).

Esterification of Methoxy- β -methoxycrotonic Acid. — When methoxy- β -methoxycrotonic acid is treated in the usual manner with alcohol and sulphuric acid or with an alcoholic solution of hydrogen chloride, decomposition takes place, and only a very small amount of the ethyl ester is obtained, the main product being ethyl acetoacetate.

It was, however, readily obtained in a pure state by the action of ethyl iodide on the silver salt of the acid. The silver salt (12 grams) was suspended in dry ether (100 c.c.), and ethyl iodide (12 grams) was added, and the solution heated on the steam-bath for three hours. After filtering from the silver iodide, the ether was removed, and the pure ester was found to boil at $109^{\circ}/18$ mm.:

0.1909 gave 0.3836 CO_2 and 0.1577 H_2O . C=54.8; H=8.0.

$\text{C}_8\text{H}_{14}\text{O}_4$ requires C=55.1; H=8.0 per cent.

The instability of this ester was clearly shown by the following experiment. The pure ester (5.26 grams) was dissolved in alcohol, and the solution saturated with dry ammonia. After twelve hours the alcohol was evaporated, when a semi-solid mass was obtained. This was drained on porous porcelain, and the solid (0.45 gram) was found to consist of ethyl dihydrolutidinedicarboxylate.

Methoxymethyl Methoxy- β -methoxycrotonate,



It has already been mentioned in the introduction that methoxy- β -methoxycrotonic acid may be distilled quite readily under diminished pressure (34 mm.), when it passes over with very slight decomposition at 158 — 160° . When, however, it is distilled under the ordinary pressure it is decomposed, some carbon dioxide being evolved, and an oil slowly passes over, the thermometer gradually rising to 220° . The oil was carefully purified by repeated distillation under 20 mm. pressure, when it was found to boil at 131 — 132° :

0.1215 gave 0.2252 CO_2 and 0.0805 H_2O . C=50.6; H=7.4.

0.0949 ,, 0.1770 CO_2 ,, 0.0664 H_2O . C=50.9; H=7.8.

$\text{C}_8\text{H}_{14}\text{O}_5$ requires C=50.5; H=7.4 per cent.

From the above analytical data, it seems probable that this oil consists of *methoxymethyl methoxy-β-methoxycrotonate*. It is a colourless, mobile oil possessing a pleasant ethereal odour. Its solution in chloroform readily absorbs bromine, and in a quantitative experiment it was found that 0.3738 gram absorbed 0.9 gram of bromine, whereas an unsaturated substance, $C_8H_{14}O_5$, should absorb 0.93 gram.

The correctness of the above constitution is supported by the fact that when the ester was hydrolysed by aqueous potassium hydroxide, a quantitative yield of methoxy-β-methoxyerotic acid was obtained.

Decomposition of Methoxy-β-methoxyerotic Acid into Acetone and Formaldehyde.—Methoxy-β-methoxyerotic acid (3 grams) was mixed with water (10 c.c.), and heated in a sealed tube for five hours at 140–150°. On opening the tube, much carbon dioxide was evolved, but only a small amount of tar had separated. The aqueous solution was distilled in steam, when a strong odour of formaldehyde was noticed, and an immediate reaction was obtained with Schiff's reagent. The steam distillate was treated with an acetic acid solution of *p*-bromophenylhydrazine, when a yellow precipitate separated. This was collected and purified by crystallisation from light petroleum, from which it separated in yellow needles, melting at 91–93°. No alteration in the melting point was noticed when it was mixed with a specimen of acetone-*p*-bromophenylhydrazone obtained from a different source.

Oxidation of Methoxy-β-methoxyerotic Acid.—The acid (2 grams) was dissolved in chloroform, and the solution treated for some hours with ozone. On removing the solvent in vacuum, a solid ozonide separated. This was decomposed by warming with water and the aqueous solution extracted with ether, the ether dried and evaporated, when a colourless oil remained. The oil gave an immediate precipitate with phenylhydrazine and *p*-bromophenylhydrazine, but all efforts to isolate a pure substance were unsuccessful; only the presence of acetic acid and formaldehyde could be definitely proved.

Ethyl αγ-Diacetylglutarate, $CO_2Et \cdot CHAc \cdot CH_2 \cdot CHAc \cdot CO_2Et$.

I. It has already been mentioned (p. 2109) that when the condensation product of monochloromethyl and ethyl sodioacetoacetate is fractionated, a heavy oil remained in the distilling flask, which apparently decomposed on distillation even under a very low pressure. It was, however, found that when it was rapidly distilled in small quantities it could readily be obtained in a pure state, and boiled quite constantly at 178°/10 mm.:

0.1154 gave 0.243 CO₂ and 0.0758 H₂O. C=57.5; H=7.3.

C₁₃H₂₀O₆ requires C=57.3; H=7.3 per cent.

Ethyl $\alpha\gamma$ -diacetylglutarate, which has not previously been obtained in a pure state, is a viscous oil possessing a slight odour reminiscent of ethyl acetoacetate. Its alcoholic solution gives an intense purple-violet coloration with ferric chloride.

That this substance consisted of ethyl $\alpha\gamma$ -diacetylglutarate was shown by the fact that on treatment with alcoholic ammonia it was converted quantitatively into ethyl dihydrolutidinedicarboxylate, which melted at 174—176° (compare Knoevenagel, *loc. cit.*).

The identity was further confirmed by hydrolysis with 10 per cent. sulphuric acid, when 1-methyl- Δ^1 -cyclohexen-3-one was obtained, which boiled, as stated by Knoevenagel, at 200—201°:

0.1419 gave 0.3952 CO₂ and 0.1175 H₂O. C=76.0; H=9.2.

C₇H₁₀O requires C=76.4; H=9.1 per cent.

The *semicarbazone* of 1-methyl- Δ^1 -cyclohexen-3-one, which does not appear to have been previously obtained, separates from water in irregular plates, melting at 201°:

0.1285 gave 0.2731 CO₂ and 0.0901 H₂O. C=57.9; H=7.8.

C₈H₁₃ON₃ requires C=57.5; H=7.8 per cent.

II. For reasons which have already been given in the introduction, the condensation of monochloromethyl ether and the copper derivative of ethyl acetoacetate was investigated, and was found to give an excellent yield of ethyl $\alpha\gamma$ -diacetylglutarate.

The copper derivative of ethyl acetoacetate (32 grams) was suspended in dry ether (200 c.c.), and monochloromethyl ether (16 grams) was added all at once. No reaction took place for some time, but later the green colour of the ethereal solution gradually disappeared, and the mixture became slightly warm. After remaining overnight, the cupric chloride was separated, and, after removing the ether, the residual oil was fractionated under 20 mm. pressure, when it distilled at 193—195°. That this substance consisted of ethyl $\alpha\gamma$ -diacetylglutarate was proved by its conversion into ethyl dihydrolutidinedicarboxylate, melting at 174—176°.

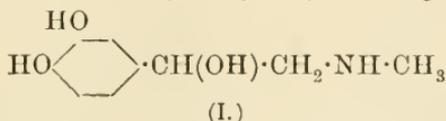
Much of the expense of this research has been met by a grant from the Research Fund Committee of the Chemical Society, for which the authors are much indebted.

THE UNIVERSITY,
MANCHESTER.

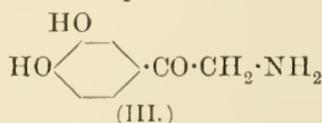
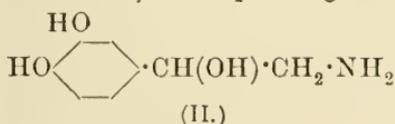
CCXXVII.—*Syntheses in the Epinephrine Series.*

By FRANK TUTIN, FREDERIC WILLIAM CATON, and
ARCHIE CECIL OSBORN HANN.

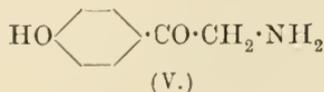
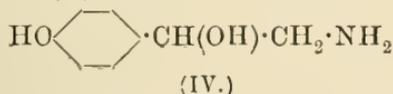
INASMUCH as the base epinephrine, which possesses a constitution represented by formula I (Jowett, *Trans.*, 1904, **85**, 192), has so valuable a physiological action, it appeared to be of considerable interest to prepare certain substances related to it, in order that their properties might be physiologically investigated:



It is already known that the ketone corresponding with epinephrine is physiologically active, as are also the primary amines (II and III) corresponding with both these compounds:



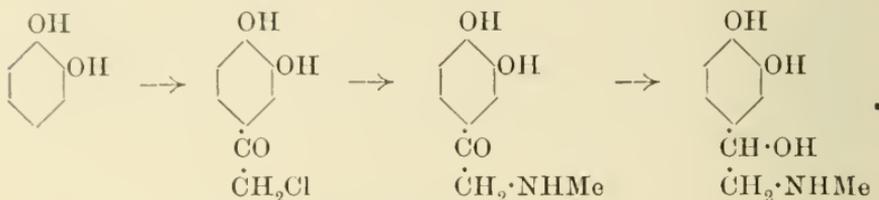
We therefore endeavoured to prepare bases analogous to the above-mentioned primary amines, but which would contain only one hydroxyl group in the benzene nucleus. This attempt has been successful, in so far as the *para*-derivatives are concerned, for *β-p*-dihydroxy-*β*-phenylethylamine (IV) and the corresponding ketone (V) have been obtained:



The physiological action of these substances has been investigated by Dr. H. H. Dale, Director of the Wellcome Physiological Research Laboratories, to whom we now express our thanks. It has thus been ascertained that both the bases (IV and V), when injected intravenously, have a pronounced influence on the blood-pressure. The intensity of the action of the keto-base is of the same order as that of the ketone corresponding with epinephrine, and it causes about one-tenth of the rise in blood-pressure produced by an equal weight of *β-p*-hydroxyphenylethylamine, $\text{HO} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2$ (Barger, *this vol.*, p. 1123). The reduction of the ketonic group in the monohydroxy-base (V) is, however, not attended with that enormous increase in activity which is observed when the ketone corresponding with epinephrine is reduced, as *β-p*-dihydroxy-

β -phenylethylamine (IV) possesses only about twice the activity of its corresponding ketone. The action of the reduced base is, however, qualitatively far more like that of epinephrine than is that of the ketonic compound.

The first synthesis of epinephrine to be described was conducted according to the following scheme (D.R.-P. 152814, 155632, and 157300):



We therefore endeavoured, in the first place, to prepare β -*p*-dihydroxy- β -phenylethylamine (IV) by a similar series of reactions, but with the employment of phenol, instead of catechol, as the initial material.

Kunckell and Johannssen (*Ber.*, 1898, **31**, 169) prepared ω -chloro-*p*-hydroxyacetophenone by the action of chloroacetyl chloride on anisole in the presence of an excess of aluminium chloride, but they failed to obtain the desired compound directly from phenol. The present authors, however, find that the chloro-ketone can be formed from phenol by means of the Friedel-Crafts reaction if nitrobenzene be employed as the solvent. The yield obtained by this method is, however, but small. The above-mentioned authors (*loc. cit.*) have shown that ω -chloro-*p*-hydroxyacetophenone chloroacetate is formed by the action of aluminium chloride and chloroacetyl chloride on phenyl chloroacetate. The present authors therefore sought to obtain the corresponding acetate in an analogous manner from phenyl acetate, as the former compound would serve equally as well as the hydroxy-ketone, from which it is derived, for the preparation of the desired amine, and the use of the relatively costly anisole would thus be avoided. It was found, however, that when a mixture of phenyl acetate and chloroacetyl chloride is treated with aluminium chloride, the acetyl group wanders into the para-position, and its place is taken by the chloroacetyl radicle, the resulting compound being *p*-hydroxyacetophenone chloroacetate (m. p. 73—74°). We therefore prepared ω -chloro-*p*-hydroxyacetophenone according to the method of Kunckell and Johannssen.

It was found impossible to obtain ω -amino-*p*-hydroxyacetophenone from the chloro-ketone by condensation with ammonia, although the experiment was conducted under a great variety of conditions. Attempts to prepare the corresponding methyl

derivative from methylamine were also unsuccessful. This result was somewhat surprising, as the corresponding dihydroxyphenyl-methylamino-ketone is formed in an analogous manner without much difficulty (D.R.-P. 155632). The only definite product that could be obtained by the action of ammonia on ω -chloro-*p*-hydroxyacetophenone was an *additive* compound, $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}_2\text{Cl}\cdot\text{NH}_3$.

The desired base, ω -*amino-p-hydroxyacetophenone* (m. p. 190—193°), was, however, eventually obtained in the following manner. ω -*Chloro-p-acetoxyacetophenone* (m. p. 89—90°) was heated with potassium phthalimide, when the *phthalyl* derivative,



(m. p. 174°), was obtained. This condensation product was then heated with concentrated hydrochloric acid, when ω -*amino-p-hydroxyacetophenone hydrochloride* was generated. The free base obtained from this salt crystallises well, and is quite stable in the absence of oxygen, a behaviour which is not at all in agreement with the statement of Gabriel (*Ber.*, 1908, **41**, 1128) that α -amino-ketones of this type cannot exist in the free state.

The next step was to reduce the ketonic group contained in the above-described base, in order to obtain the final product. It was found, however, that this could not be accomplished in a manner analogous to that by which epinephrine was obtained from its corresponding ketone, namely, by the action of aluminium amalgam. The behaviour of other reducing agents was therefore investigated, when it was found that the desired result was attained by the use of sodium and alcohol. The β -*p*-dihydroxy- β -phenylethylamine (IV) so obtained darkened and absorbed oxygen rapidly on exposure to the air, and could not be crystallised, and this was also the case with its hydrochloride. It readily yielded, however, a crystalline *tribenzoyl* derivative (m. p. 182°), by means of which the identity of the substance was verified.

At the stage in this work when it was found that the desired ketonic base could not be obtained by the action of ammonia on the corresponding chloro-compound, it was thought that the object might be attained by the method first employed by Jowett (*Trans.*, 1905, **87**, 967) for syntheses in the epinephrine series, which has since been used with some success by others (Böttcher, *Ber.*, 1909, **42**, 253; Pauly and Neukam, *Ber.*, 1908, **41**, 4151; Mannich and Jacobson, *Chem. Zeitsch.*, 1909, **33**, 923). For this purpose we endeavoured to prepare α -hydroxy-*p*-methoxy- α -phenylethane, in order that, by the elimination of water from this compound, *p*-vinylphenol might be obtained. *p*-Hydroxyacetophenone was therefore reduced, but this only resulted in the formation of a

pinacone (m. p. 207—208°). We then prepared α -*p*-hydroxyphenylethylamine by the reduction of *p*-hydroxyacetophenoneoxime. The base was subsequently heated with nitrous acid, but the resulting product, which presumably contained α -*p*-dihydroxy- α -phenylethane, was very unstable when exposed to the air, rapidly yielding acetaldehyde and a brown resin.

α -*p*-Hydroxyphenylethylamine possesses special interest, inasmuch as it was found to have a physiological action similar to that exerted by its β -isomeride, which has been shown by Barger (*loc. cit.*) to be one of the active principles of ergot. The naturally occurring compound is, however, very considerably more active. An attempt was furthermore made to prepare *p*-vinylphenol by the dry distillation of *p*-coumaric acid, under the same conditions as lead to the formation of the corresponding ortho-compound (*Ber.*, 1908, **41**, 367), but only polymerised products could be obtained.

As we were unsuccessful in preparing *p*-vinylphenol, *p*-vinylanisole (Klages, *Ber.*, 1903, **36**, 3590) was employed. From the latter, the *dibromide* (m. p. 80—81°) was obtained, and this, by means of aqueous acetone, was converted into the *bromohydrin*, $\text{MeO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Br}$, which is a liquid. No satisfactory method, however, could be devised of converting the latter compound into the corresponding amine, the yields of basic product being extremely small. It is interesting to note that on treatment with acetyl chloride, the hydroxyl group in the bromohydrin is replaced by chlorine, the resulting α -chloro- β -bromo-*p*-methoxy- α -phenylethane, $\text{MeO}\cdot\text{C}_6\text{H}_4\cdot\text{CHCl}\cdot\text{CH}_2\text{Br}$, being a solid, melting at 39—40°. It has been stated by Muset (*Bull. Acad. roy. Belg.*, 1906, 775) that the replacement of hydroxyl by chlorine through the agency of acetyl chloride is characteristic of tertiary alcohols, but the above change shows that this is not always the case.

Some experiments were also made with the object of obtaining ortho- and meta-compounds corresponding with the above-described β -*p*-dihydroxy- β -phenylethylamine. *o*-Vinylphenol was prepared by the dry distillation of *o*-coumaric acid, but no dibromide could be obtained from it. *m*-Vinylphenol was prepared from *m*-nitrocinnamic acid, according to the method of Komppa (*Ber. Ref.*, 1893, **26**, 677), but the yield of the final product was so small that we did not proceed further in this direction. The derivatives of *m*-aminostyrene thus obtained did not, however, agree in their properties with the corresponding substances described by Komppa (*loc. cit.*). The last-mentioned author appears to have regarded the hydrochloride and benzoyl derivative as being anhydrous, and stated that the latter substance fused at 90—91°. These compounds, as prepared by the present authors, do not crystallise

except with one molecule of water, and melt respectively at 181° and $126-127^{\circ}$.

EXPERIMENTAL.

ω-Chloro-p-hydroxyacetophenone.

Kunckell and Johannssen (*Ber.*, 1898, **31**, 167) prepared *ω*-chloro-*p*-hydroxyacetophenone by the action of chloroacetyl chloride and excess of aluminium chloride on anisole, but, when they attempted to obtain it directly from phenol, the experiment resulted in the formation of phenyl chloroacetate, and subsequently of *ω*-chloro-*p*-hydroxyacetophenone chloroacetate. With the object of obtaining from phenol the acetate corresponding with the last-mentioned compound, the present authors treated phenyl acetate with chloroacetyl chloride and aluminium chloride.

Thirteen grams of phenyl acetate and an equal weight of chloroacetyl chloride were dissolved in carbon disulphide, and treated with 17 grams of powdered aluminium chloride. After heating the mixture for six hours, the solvent was removed, and ice and dilute hydrochloric acid were added. The product was then extracted with ether, when, on removing the solvent, a light green oil was obtained, which became partly solid when stirred with light petroleum. The solid was drained on a tile, after which it was recrystallised from benzene, when colourless needles, melting at $73-74^{\circ}$, were obtained:

0.1869 gave 0.3850 CO_2 and 0.0729 H_2O . C=56.2; H=4.3.

$\text{C}_{10}\text{H}_9\text{O}_3\text{Cl}$ requires C=56.5; H=4.2 per cent.

That this compound was *p*-hydroxyacetophenone chloroacetate was evident from the fact that, on treatment with ammonia, it yielded *p*-hydroxyacetophenone and the base,



which was obtained by Heintz by the action of ammonia on ethyl chloroacetate (*Annalen*, 1868, **148**, 177). It is evident, therefore, that the acetyl group had wandered into the para-position, its place being taken by the chloroacetyl radicle.

In view of the statements of Behn (D.R.-P. 95901), we attempted to obtain *ω*-chloro-*p*-hydroxyacetophenone directly from phenol by means of aluminium chloride, but with the use of nitrobenzene as a solvent. Although this operation was successful, the yield was so small that we returned to the original method of Kunckell and Johannssen (*loc. cit.*), using, however, an improved means of isolating the product.

Twenty grams of anisole and 24 grams of chloroacetyl chloride were dissolved in carbon disulphide, and 60 grams of aluminium chloride gradually introduced. After heating for about four hours,

the solvent was removed, the residue treated with ice and hydrochloric acid, and the product extracted with ether. The ethereal liquid thus obtained was shaken with a solution of ammonium carbonate, which removed a small amount of brown product, after which it was treated with aqueous sodium carbonate. This removed the *o*-chloro-*p*-hydroxyacetophenone in a state of relative purity. During these operations a most severe irritation of the eyes and face was experienced. This was found to be due to the formation of a small amount of *o*-chloro-*o*-methoxyacetophenone, a substance which will be described in a subsequent communication. The sodium carbonate extracts were acidified, and the precipitated product crystallised from methyl alcohol, when *o*-chloro-*p*-hydroxyacetophenone was obtained in the form of light yellow laminae, melting at 148°.

Action of Ammonia and Methylamine on o-Chloro-p-hydroxyacetophenone.

A quantity of *o*-chloro-*p*-hydroxyacetophenone was dissolved in alcohol, and a solution of ammonia in absolute alcohol added. The mixture became red, some heat being developed, and a crystalline substance soon separated. The latter was collected, and recrystallised from an alcoholic solution of ammonia. It was then found to be an *additive* compound of the chloro-ketone and one molecule of ammonia, the latter being held only rather loosely:

0.3010, dissolved in alcohol, neutralised 16.0 c.c. *N*/10-H₂SO₄.
NH₃ = 9.0.

C₈H₇O₂Cl.NH₃ requires NH₃ = 9.1 per cent.

On keeping this substance for any considerable length of time in contact with aqueous or alcoholic ammonia, or on heating it with either of these reagents, only red, tarry products resulted. This was also the case when only the theoretical amount of ammonia was employed. Analogous experiments, conducted with the use of methylamine, likewise resulted only in the formation of red, amorphous products.

Condensation of o-Chloro-p-acetoxyacetophenone with Potassium Phthalimide.

Since it was found impossible to obtain an amine from the chloro-ketone by condensation with ammonia, recourse was had to the use of potassium phthalimide. It was found necessary, however, to employ the acetyl derivative of the chloro-ketone, since the original substance was so acidic that it decomposed the potassium phthalimide.

ω -Chloro-*p*-hydroxyacetophenone was boiled for one hour with acetic anhydride, and the resulting acetylated product purified by distillation. ω -Chloro-*p*-acetoxyacetophenone crystallises from alcohol in large prisms, which melt at 89—90°:

0.1553 gave 0.3218 CO₂ and 0.0592 H₂O. C = 56.5; H = 4.2.

C₁₀H₉O₃Cl requires C = 56.5; H = 4.2 per cent.

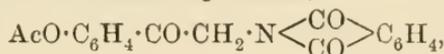
After numerous experiments, the following method of condensing the acetyl derivative of the chloro-ketone with potassium phthalimide was found to be the best, a yield of phthalide derivative amounting to about 42 per cent. of that theoretically possible being obtained. ω -Chloro-*p*-acetoxyacetophenone was heated in a nickel crucible to 120—125°, when a molecular proportion of finely-powdered potassium phthalimide was gradually introduced, with constant stirring. The mixture, which was at first quite fluid, gradually became viscid, and, after being maintained at the above temperature for about half an hour, was completely converted into a brown solid. The latter, after being powdered, was extracted in a Soxhlet apparatus with boiling benzene. On concentrating the benzene extract, the condensation product, together with phthalimide, separated in crystals. The solid was collected, washed with benzene, and freed from phthalimide by repeated extraction with boiling water, after which the phthalide derivative was crystallised from alcohol. It then formed slender, colourless needles, melting at 174°:

0.1476 gave 0.3627 CO₂ and 0.0574 H₂O. C = 67.0; H = 4.3.

0.3785 ,, 14.8 c.c. N₂ (moist) at 20.8° and 766 mm. N = 4.5.

C₁₈H₁₃O₅N requires C = 66.9; H = 4.0; N = 4.3 per cent.

p-Acetoxy- ω -phthaliminoacetophenone,



is rather sparingly soluble in alcohol, but more readily soluble in benzene, ethyl acetate, or glacial acetic acid. It is insoluble in water or light petroleum.

\omega-Amino-*p*-hydroxyacetophenone.

The above-described phthalide derivative (2 parts), together with glacial acetic acid (15 parts) and concentrated hydrochloric acid (50 parts), was heated in sealed tubes to 130° for three hours. The contents of the tubes, which had become brown, were united, concentrated under diminished pressure, and freed from phthalic acid by extraction with ether. The liquid was then treated with animal charcoal, filtered, and evaporated to dryness under diminished pressure, as it is necessary to avoid the access of air

so far as possible. The dry residue was dissolved in alcohol, and after some time *ω*-amino-*p*-hydroxyacetophenone hydrochloride separated in pink prisms, which were obtained colourless by further recrystallisation from alcohol. This hydrochloride dissolves very readily in water, but only moderately so in alcohol, and not at all in ethyl acetate. It has no definite melting point, but decomposes at 245—252°:

0.2644 gave 0.1982 AgCl. Cl=18.6.

$C_8H_9O_2N, HCl$ requires Cl=18.9 per cent.

ω-Amino-*p*-hydroxyacetophenone was obtained from the aqueous solution of its hydrochloride by precipitation with sodium carbonate. It forms colourless plates, which melt and decompose at 190—193°:

0.0982 gave 0.2278 CO_2 and 0.0546 H_2O . C=63.4; H=6.2.

0.1137 „ 0.2660 CO_2 „ 0.0644 H_2O . C=63.8; H=6.3.

$C_8H_9O_2N$ requires C=63.6; H=6.0 per cent.

It is only with difficulty that this base can be obtained colourless, as in contact with air and moisture, especially in alkaline solutions, it rapidly acquires a brilliant pink colour. It is readily soluble in both acids and alkali hydroxides, very sparingly so in water, alcohol, or ethyl acetate, and insoluble in chloroform or ether. It yields a *picrate*, which crystallises in needles, melting at 192°, but its gold and platinum salts were too soluble to admit of their isolation.

ω-Benzoylamino-*p*-benzoyloxyacetophenone,



was prepared by the Schotten-Baumann method. It forms colourless needles, melting at 173—174°:

0.0992 gave 0.2685 CO_2 and 0.0439 H_2O . C=73.8; H=4.9.

$C_{22}H_{17}O_4N$ requires C=73.6; H=4.7 per cent.

β-*p*-Dihydroxy-*β*-phenylethylamine.

Attempts were first made to reduce *ω*-amino-*p*-hydroxyacetophenone by means of aluminium amalgam, in a manner similar to that by which epinephrine has been obtained from its corresponding ketone (D.R.-P. 157300), but, although some change was effected by this means, the desired result was not attained. It was found, however, that sodium and boiling alcohol is a satisfactory reducing agent for this purpose.

Five grams of *ω*-amino-*p*-hydroxyacetophenone hydrochloride were dissolved in 250 c.c. of absolute alcohol in a flask attached to a reflux condenser, and 30 grams of metallic sodium gradually introduced in small pieces, under such conditions that the liquid was kept in a state of rapid ebullition. When the metal had

dissolved, the mixture was quickly cooled, after which concentrated hydrochloric acid was added until the liquid ceased to be alkaline to litmus. The precipitated sodium chloride was then removed, the filtrate evaporated to dryness under diminished pressure, and the residue extracted with absolute alcohol. In this way, the remaining small amount of sodium chloride was removed. The alcoholic extracts were concentrated, ethyl acetate added, and the resulting mixture again evaporated. A relatively small amount of the unchanged hydrochloride then separated in a crystalline condition, and was removed. The filtrate contained a *hydrochloride*, which was nearly insoluble in ethyl acetate, but could not be induced to crystallise. When dissolved in water, this salt absorbed oxygen, even at the ordinary temperature, and this change occurred rapidly on evaporating the aqueous solution with the aid of heat. On rendering the solution of the salt alkaline with sodium carbonate, a base was precipitated, but this substance, like its hydrochloride, could not be crystallised, and it rapidly absorbed oxygen. The identity of this base as β -*p-dihydroxy- β -phenylethylamine* was, however, proved by means of its benzoyl derivatives.

A quantity of the aqueous solution of the reduced hydrochloride was benzoylated by means of the Schotten-Baumann reaction. The product so obtained was crystallised from alcohol, when it melted at 145—175°, and obviously consisted of a mixture. By crystallisation from benzene, it was ultimately separated into two substances, the more readily soluble of which formed slender needles, melting at 182°:

0.0999 gave 0.2737 CO₂ and 0.0461 H₂O. C = 74.7; H = 5.1.

C₂₉H₂₃O₅N requires C = 74.8; H = 4.9 per cent.

0.3110 in 30.6 of nitrobenzene gave Δt = 0.170°. M.W. = 419.

0.3572 „ 35.0 „ „ „ „ Δt = 0.170°. M.W. = 420.

C₂₉H₂₃O₅N requires M.W. = 465.

It is evident from the above results that this substance was the *tribenzoyl* derivative of β -*p-dihydroxy- β -phenylethylamine*, BzO·C₆H₄·CH(OBz)·CH₂·NHBz, the molecular weight determinations clearly showing that it could not be a derivative of a pinacone.

The more sparingly soluble constituent of the above-described mixture melted at 210°, and, when pure, formed glistening leaflets, which were nearly insoluble in benzene. It proved to be a *dibenzoyl* derivative corresponding with the above-mentioned tribenzoyl compound, since it readily yielded the latter on further treatment with benzoyl chloride. Moreover, since the tribenzoyl derivative, when boiled with 80 per cent. alcohol, yielded this

dibenzoyl compound, melting at 210°, it would appear that the latter possesses the structure $\text{BzO} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{NHBz}$:

0.1017 gave 0.2736 CO_2 and 0.0486 H_2O . C=73.4; H=5.3.

0.1070 „ 0.2860 CO_2 „ 0.0500 H_2O . C=72.9; H=5.2.

$\text{C}_{22}\text{H}_{19}\text{O}_4\text{N}$ requires C=73.1; H=5.3 per cent.

The results of the physiological experiments, recorded in the introductory portion of this paper, also afford confirmation of the fact that β -*p*-dihydroxy- β -phenylethylamine had been formed by the reduction of the ω -amino-*p*-hydroxyacetophenone, although the former compound could not be isolated in a state of purity.

As previously stated, attempts were made to prepare some of the above-described compounds by other means. Although the desired results were not thus attained, these experiments led to the production of a variety of new compounds, which are described below.

p-Hydroxyacetophenone was reduced by means of sodium amalgam, both in alkaline and acid solutions, and also by aluminium amalgam. The greater part of the product was, in each case, a viscid oil, but a crystalline solid was also formed, the amount of the latter being greatest when the neutral reducing agent was employed.

Twenty grams of *p*-hydroxyacetophenone were dissolved in a large volume of aqueous methyl alcohol, and a quantity of aluminium amalgam added. The mixture was kept, with occasional stirring, until the aluminium had disappeared, when the product was extracted with ether. The material obtained after removing the solvent was dissolved in ethyl acetate, when 7.5 grams of a solid, in the form of a crystalline powder, gradually separated. This product was crystallised from alcohol, when it formed small, colourless prisms, which melted at 207—208°. It was sparingly soluble in alcohol and in water, and nearly insoluble in ethyl acetate:

0.1523 gave 0.3908 CO_2 and 0.0914 H_2O . C=69.6; H=6.7.

$\text{C}_8\text{H}_{10}\text{O}_2$ requires C=69.6; H=7.2 per cent.

$\text{C}_{16}\text{H}_{18}\text{O}_4$ „ C=70.1; H=6.6 „

This substance proved to be the *pinacone*, $\text{C}_{16}\text{H}_{18}\text{O}_4$, and not the desired secondary alcohol, as shown by the molecular weight of its *tetra-acetyl* derivative. The latter compound, formed in the usual way, crystallised from alcohol in colourless leaflets, which melted at 188—189°:

0.1293 gave 0.3086 CO_2 and 0.0710 H_2O . C=65.1; H=6.1.

$\text{C}_{24}\text{H}_{26}\text{O}_8$ requires C=65.2; H=5.9 per cent.

0·1760 in 19·5 of benzene gave $\Delta t - 0\cdot125^\circ$. M.W. = 410.

0·1098 „ 22·2 „ naphthalene gave $\Delta t - 0\cdot080^\circ$. M.W. = 426.

$C_{24}H_{26}O_8$ requires M.W. = 442.

α -p-Hydroxyphenylethylamine.

Eight grams of *p*-hydroxyacetophenoneoxime (m. p. 144—145°) were dissolved in 100 c.c. of aqueous methyl alcohol, and twice the theoretical amount of 2 per cent. sodium amalgam gradually introduced in small pieces, the mixture being constantly maintained acid by the frequent addition of acetic acid. When all reaction had ceased, the liquid was extracted with ether to remove unchanged oxime, after which it was rendered alkaline by means of potassium carbonate, and repeatedly extracted with amyl alcohol. The resulting amyl-alcoholic liquids were extracted with successive quantities of dilute hydrochloric acid, and the combined acid liquids concentrated under diminished pressure. *α -p-Hydroxyphenylethylamine hydrochloride* then separated in stout prisms, which were purified by recrystallisation from water. This salt is soluble in alcohol, and insoluble in ethyl acetate; it possesses no definite melting point, but gradually softens, and darkens at 200—280°. Above the latter temperature it yields a sublimate of ammonium chloride, together with phenol, but it was ascertained that no *p*-vinylphenol was formed:

0·1527 gave 0·3086 CO_2 and 0·0964 H_2O . C = 55·1; H = 7·0.

$C_9H_{12}ONCl$ requires C = 55·4; H = 6·9 per cent.

α -p-Hydroxyphenylethylamine, as obtained from its hydrochloride, was sparingly soluble in water or alcohol, and insoluble in ether or chloroform. It formed an amorphous, gum-like mass, which could not be crystallised.

The *dibenzoyl* derivative, prepared by the Schotten-Baumann method, crystallises from dilute alcohol in fine needles, and melts at 187—188°:

0·1528 gave 0·4280 CO_2 and 0·0758 H_2O . C = 76·4; H = 5·5.

$C_{22}H_{19}O_3N$ requires C = 76·5; H = 5·5 per cent.

α -p-Hydroxy-N-benzoylphenylethylamine, $HO\cdot C_6H_4\cdot CHMe\cdot NHBz$, was formed on heating the *dibenzoyl* derivative with 5 per cent. alcoholic potash. It crystallises from alcohol in large, hexagonal prisms, melting at 156°:

0·1125 gave 0·3096 CO_2 and 0·0631 H_2O . C = 75·0; H = 6·2.

$C_{15}H_{15}O_2N$ requires C = 74·8; H = 6·2 per cent.

Several attempts were made to prepare *α -p-dihydroxy- α -phenylethane* by the action of heat on the nitrite of *α -p-hydroxyphenylethylamine*, but the products so obtained were very unstable in the

presence of air, rapidly yielding acetaldehyde and a brown resin. An experiment was therefore conducted in an atmosphere of carbon dioxide, and the product immediately acetylated by means of acetic anhydride. An oil was thus obtained, which distilled at about 200°/20 mm., and, on analysis, yielded the following result:

0.1522 gave 0.3723 CO₂ and 0.0916 H₂O. C=66.7; H=6.7.

C₁₀H₁₂O₃ requires C=66.7; H=6.6 per cent.

It would thus appear that this liquid was a *monoacetyl* derivative of *α-p-dihydroxy-α-phenylethane*.

p-Vinylanisole Derivatives.

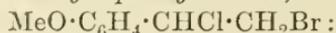
α-Hydroxy-p-methoxy-α-phenylethane was prepared from anisaldehyde by means of the Grignard reaction, and, with the use of hydrochloric acid, was converted into the chloride. The latter, on treatment with pyridine, forms *p-vinylanisole* (Klages, *Ber.*, 1903, **36**, 3595).

αβ-Dibromo-p-methoxy-α-phenylethane, MeO·C₆H₄·CHBr·CH₂Br, was formed by the gradual addition of a cold ethereal solution of bromine to a solution of *p-vinylanisole* in the same solvent, cooled in ice. The new compound, which separates from the ether, was purified by recrystallisation from light petroleum, when it formed long, prismatic needles, melting at 80—81°:

0.1351 gave 0.1710 AgBr. Br=53.9.

C₉H₁₀OBr₂ requires Br=54.4 per cent.

In order to convert the above dibromo-derivative into the bromohydrin, MeO·C₆H₄·CH(OH)·CH₂Br, it was dissolved in acetone containing 10 per cent. of its weight of water, and the solution kept at the ordinary temperature (Auwers and Miller, *Ber.*, 1902, **35**, 114). It was ascertained, by titrating at intervals aliquot portions of the mixture, that the reaction proceeded regularly, and was completed quantitatively at the end of about seven and a-half hours. On isolating the bromohydrin, however, this compound was found to be a liquid. Nevertheless, the exact quantitative character of the change left no doubt regarding the nature of the product. With the endeavour to prepare an acetyl derivative from the liquid bromohydrin, the latter was heated with acetyl chloride. This resulted in the formation of a solid, which crystallised from light petroleum in needles, melting at 39—40°, and proved to be *α-chloro-β-bromo-p-methoxy-α-phenylethane*,



0.2223 gave 0.2939 AgBr + AgCl. Br + Cl=46.0.

C₉H₁₀OClBr requires Br + Cl=46.3 per cent.

The bromohydrin was treated with ammonia under a great variety of conditions, but only small amounts of basic products

could be obtained, even when anhydrous, liquid ammonia was employed. The chief products were, in every case, resinous materials and volatile, unsaturated oils. Experiments with the use of potassium phthalimide were equally unsuccessful. The small yields of basic products which were obtained from the bromohydrin by means of ammonia were fractionally precipitated as picrate. In this manner it was found that at least two compounds were present, one of which yielded a *picrate*, forming flattened needles, melting at 215° . The *base* from the latter crystallised from benzene in cubes, which melted at $165\text{--}166^{\circ}$:

0.0520 gave 0.1394 CO_2 and 0.0348 H_2O . $\text{C}=73.1$; $\text{H}=7.4$.

$\text{C}_9\text{H}_{11}\text{ON}$ requires $\text{C}=72.5$; $\text{H}=7.3$ per cent.

It would thus appear probable that this compound was the base, $\text{MeO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{NH}_2$.

The other *picrate* obtained formed stout prisms, melting at 188° , and the corresponding *base* yielded a *benzoyl* derivative crystallising in needles, which fused at 108° , but the amounts were too small for analysis.

m-Aminostyrene.

m-Aminostyrene was prepared from *m*-nitrobenzaldehyde by Komppa's method (*loc. cit.*). It was converted into its hydrochloride by passing dry hydrogen chloride into the dry ethereal solution of the base. The salt thus obtained could not be crystallised until water was introduced. The latter was then absorbed, with the evolution of heat, when crystallisation rapidly ensued. The product so obtained was crystallised from alcohol, and then formed well-defined prisms, which melted at 181° :

0.1342, dried at 100° , gave 0.2705 CO_2 and 0.0581 H_2O . $\text{C}=55.0$;
 $\text{H}=7.0$.

0.3506 gave 0.2870 AgCl . $\text{Cl}=20.3$.

$\text{C}_8\text{H}_9\text{N}\cdot\text{HCl}\cdot\text{H}_2\text{O}$ requires $\text{C}=55.3$; $\text{H}=6.9$; $\text{Cl}=20.3$ per cent.

Although the water present in this hydrochloride was not expelled at 150° , it was, nevertheless, retained as water of crystallisation. This was shown by the fact that the amorphous, anhydrous hydrochloride was again obtained from the regenerated base by treatment with dry hydrogen chloride.

Benzoylaminostyrene, prepared by the Schotten-Baumann method, crystallises from alcohol in hexagonal plates, melting at $126\text{--}127^{\circ}$, and, like the foregoing compound, tenaciously retains one molecule of water of crystallisation:

0.1377, dried at 130° , gave 0.3755 CO_2 and 0.0796 H_2O . $\text{C}=74.4$;
 $\text{H}=6.4$.

0.0998, dried at 130°, gave 0.2747 CO₂ and 0.0586 H₂O. C = 75.1 ;
H = 6.5.

CH₂:CH·C₆H₄·NH·CO·C₆H₅, H₂O requires C = 74.7 ; H = 6.2 per cent.

Komppa (*loc. cit.*) apparently regarded this compound as being anhydrous, and stated that it melted at 90—91°.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C.

CCXXVIII.—*A New Method for the Detection of Sodium, Caesium, and Rubidium.*

By WALTER CRAVEN BALL.

IN a former paper (Trans., 1905, **87**, 761), the author described several complex nitrites of bismuth, prepared from the yellow liquid obtained by the interaction of sodium nitrite and bismuth nitrate. Among the compounds described were bismuth sodium ammonium nitrite, Bi(NO₂)₃, 2NH₄NO₂, NaNO₂, and bismuth potassium nitrite, Bi(NO₂)₃, 3KNO₂, H₂O, both very soluble compounds. On endeavouring to prepare similar rubidium and caesium derivatives, it was found that dilute solutions of the nitrates of these metals produced yellow, crystalline precipitates with the reagent obtained from sodium nitrite and bismuth nitrate. These are triple nitrites of bismuth, sodium, and rubidium or caesium, and their formation serves as a very useful method for detecting these metals in presence of excess of potassium. The reaction for caesium is especially delicate.

When, however, rubidium and caesium nitrates were added to the reagent obtained from potassium nitrite and bismuth nitrate, instead of from sodium nitrite and bismuth nitrate, the results were very different. Rubidium nitrate produced no precipitate, even when a concentrated solution was used, whilst caesium produced a precipitate, even when added in dilute solution, yet this precipitate was very much smaller in amount than that obtained by adding the same quantity of caesium salt to the bismuth-sodium nitrite reagent. The precipitate from caesium nitrate and the bismuth-potassium nitrite reagent was then examined, and was found to be the triple nitrite of bismuth, sodium, and caesium, mentioned above, and was quite free from potassium.

It was evident that the potassium nitrite used (Kahlbaum's purest) contained sodium nitrite, and that the bismuth-potassium

nitrite reagent, to which cæsium nitrate had been added, would be a delicate reagent for sodium in the presence of much potassium. It is necessary to use potassium nitrite as free as possible from sodium, as otherwise much cæsium is wasted in precipitating this when making up the reagent as a test for sodium. Kahlbaum's purest potassium nitrite was unsuitable for this purpose, as, although it was free from hydrate and nitrate, yet it contained about 1 per cent. of sodium nitrite, much more than is contained in the sticks of nitrite obtained from several other sources.

The exact methods of testing for rubidium, cæsium, and sodium are described below, together with the limits of the tests.

The bismuth-sodium nitrite reagent is best prepared by dissolving 50 grams of pure sodium nitrite in 100 c.c. of water, neutralising with nitric acid if necessary, and then adding 10 to 20 grams of powdered bismuth nitrate. The orange-coloured solution of bismuth-sodium nitrite must then be filtered, and kept in a well-stoppered bottle, as it absorbs oxygen, and becomes turbid when exposed to the air.

The reagent is hydrolysed by the addition of an excess of water, with production of a white precipitate; and although this may be prevented by adding dilute nitric acid at the same time, the delicacy of the reagent is slightly diminished. It is therefore necessary to add the solution to be tested to a large excess of the reagent, acidified with one or two drops of dilute nitric acid. If the solution to be tested is dilute, the precipitate may take some time to form; in this case, the mixture should be kept from contact with the air in a well-stoppered vessel, in order to avoid any turbidity caused by oxidation. Should the liquid have become at all turbid, it may be cleared by the addition of one or two drops of dilute nitric acid.

In testing for sodium, as described below, the same precautions must be observed.

If the salt to be tested is a chloride, its concentration should be less than 1 per cent., as otherwise bismuth oxychloride may precipitate and interfere with the test. In the case of rubidium, it is best to convert the chloride into the nitrate, which can be done by evaporating once with strong nitric acid.

Nitrates and sulphates may be used in any concentration.

Detection of Rubidium.

On addition of 1 c.c. of a 2 per cent. solution of rubidium nitrate to 4 or 5 c.c. of the bismuth-sodium nitrite reagent, acidified with a few drops of dilute nitric acid, a bright yellow, crystalline precipitate forms at once.

With a 0.5 per cent. solution, precipitation also occurs quickly, but a concentration half as great as this only gives a slight precipitate.

Only the heavy metals and caesium interfere. The test thus affords an easy method for distinguishing rubidium from potassium, ammonium, lithium, thallium, etc., which give no similar precipitates with the reagent.

The precipitate formed is bright yellow and crystalline. It is not altered on heating at 100° , but, like all the bismuth nitrite derivatives, it is decomposed by water and dilute acids. It is a triple nitrite of bismuth, rubidium, and sodium, and gave, on analysis, $\text{NO}_2=40.40$ per cent. As mentioned above, no similar precipitate is obtained on adding a rubidium salt to the bismuth-potassium nitrite reagent, but if to this mixture a solution of sodium nitrate be added, the same triple nitrite is thrown down. Prepared in this way, it gave, on analysis, $\text{NO}_2=40.74$.

$\text{Bi}(\text{NO}_2)_3, 2\text{RbNO}_2, \text{NaNO}_2$ requires $\text{NO}_2=40.71$ per cent.

The substance is thus probably similar in formula to the bismuth sodium ammonium nitrite described in the former paper, and mentioned above.

Detection of Caesium.

The same bismuth-sodium nitrite reagent serves also as a much more delicate test for caesium.

One c.c. of a 0.2 per cent. solution of caesium nitrate gives an immediate yellow, crystalline precipitate with 4 or 5 c.c. of the reagent.

One c.c. of a 0.02 per cent. solution does not produce an immediate precipitate, but one forms after several hours. A fifth of a milligram of caesium in 1 c.c. is thus capable of being detected.

The limitations of the test are similar to those in the case of rubidium. The precipitate is a bright yellow, crystalline powder, very similar to, but lighter in colour than, the rubidium compound. It is identical with the compound formed on adding a sodium salt to a mixture of the bismuth-potassium nitrite reagent and caesium nitrate, and its composition, apparently rather complex, is considered in the next section.

Detection of Sodium.

A very delicate reagent for the detection of sodium is obtained by dissolving 50 grams of potassium nitrite (as free as possible from sodium) in 100 c.c. of water, neutralising with nitric acid, and adding 10 grams of powdered bismuth nitrate. To this liquid, after filtration, a 10 per cent. solution of caesium nitrate is added until the powdery, yellow precipitate invariably produced (due to traces of sodium in the potassium nitrite) ceases to be formed

on keeping the liquid for several hours. The liquid is then filtered, and the addition of the caesium continued until the total amount of caesium salt used is about 2.5 grams. If the potassium nitrite used should contain much sodium salt, a correspondingly larger amount of the caesium salt must be added. The reagent is most sensitive when a precipitate of yellow, hexagonal plates (due to a nitrite of bismuth and caesium) forms on further addition of the caesium salt. The total volume of the reagent prepared in this way should be about 150 c.c. The proportions may be varied, but those given seem to give the most satisfactory results. The reagent must be exposed to the air as little as possible and, if turbid, it must be filtered before use.

One per cent. solutions of sodium nitrate or sulphate give an immediate yellow, crystalline precipitate with the reagent acidified with a few drops of dilute nitric acid. Solutions of half this strength also produce an almost immediate precipitate.

0.1 c.c. of a 0.5 per cent. solution of sodium (as nitrate) gave a considerable precipitate within five minutes with 2 c.c. of the reagent.

0.1 c.c. of a 0.1 per cent. solution of sodium (as nitrate) gave with 2 c.c. of the reagent a satisfactory precipitate within thirty minutes.

0.5 c.c. of a 0.01 per cent. solution of sodium (as nitrate) (=0.00005 gram of sodium) gave with 2 c.c. of the reagent a precipitate within twelve hours.

0.1 c.c. of a 0.01 per cent. solution of sodium (as nitrate) (=0.00001 gram of sodium) gave with 2 c.c. of the reagent a precipitate within twelve hours; this was easily visible to the naked eye, and, under the microscope, was seen to consist of a large number of characteristic, minute, yellow crystals (octahedra?).

Thus, about 0.01 milligram of sodium can be easily detected by this test in the presence of much potassium salt. With the potassium antimonate test for sodium, it is difficult to obtain a satisfactory precipitate of acid sodium pyroantimonate when the concentration of sodium salt is much less than 1 per cent., and almost all the other metals, including calcium, barium, lithium, and ammonium interfere with the test.

Most of the heavy metals interfere when testing for sodium with the bismuth-caesium reagent, as they produce precipitates of double bismuth nitrites, which are often highly crystalline. Some of these, particularly the silver compound, have been obtained in a pure state. Cobalt interferes owing to the production of insoluble caesium cobaltinitrite. Nickel salts produce a brown, microcrystalline precipitate. Zinc, cadmium, magnesium, barium, calcium, strontium, lithium, thallium, and potassium do not inter-

ferre. Ammonium salts do so only in so much as they react with the nitrous acid of the reagent, giving rise to an evolution of nitrogen, but it is easy to detect a milligram of sodium salt in presence of a gram of ammonium nitrate.

The composition of the yellow precipitate obtained in testing for sodium was not easily ascertained. The analytical results did not agree well with the formula $\text{Bi}(\text{NO}_2)_3, 2\text{CsNO}_2, \text{NaNO}_2$, which might have been expected from analogy, and the fact that the ratio between the cæsium and sodium was 3 atoms of cæsium to 2 of sodium, made the following formula the only possible one:



The analytical results given below, which are the means of several results, are in very good agreement, except as regards the bismuth, which is too high. It will be noticed that the number of NO_2 groups combined with the bismuth and with the sodium and cæsium is the same.

	Bi, per cent.	NO_2 , per cent.	Cs + Na, per cent.	Equivalent of the mixture of Cs + Na.
Found	28·4	37·3	36·05	88·9
	28·3	36·1		
	28·4	36·6		
	—	36·4		
	Mean = 28·38	Mean = 36·6		
$5\text{Bi}(\text{NO}_2)_3, 9\text{CsNO}_2, 6\text{NaNO}_2$ requires	27·7	36·7	35·6	$\frac{9\text{Cs} + 6\text{Na}}{15} = 89$

Quantitative Determination of Sodium by Means of the Reagent.

Preliminary experiments have been made, which indicate that small quantities of sodium, whether present as nitrate, sulphate, or chloride, may be accurately estimated by the above method.

(1) Sodium nitrate used = 2 c.c. of a solution containing 0·004944 gram of sodium per c.c. = 0·00989 gram Na. Precipitate = 0·2675 gram. $5\text{Bi}(\text{NO}_2)_3, 9\text{CsNO}_2, 6\text{NaNO}_2$ contains Na = 3·675 per cent. Hence Na found = 0·00983 gram.

(2) Sodium chloride used = 2 c.c. of a solution containing 0·003143 gram of sodium per c.c. = 0·0063 gram Na. Precipitate = 0·1658 gram. Hence Na found = 0·0061 gram.

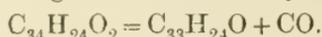
(3) Determination of sodium in Kahlbaum's special potassium nitrite. 0·893 gram gave 0·0630 gram precipitate. Hence Na found = 0·00232 gram, or $\text{NaNO}_2 = 0·00695$ gram = 0·78 per cent.

The author is at present making a more complete study of the quantitative estimation of sodium by this method, and hopes to present a further communication with regard to it.

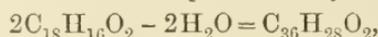
acid (Japp and Burton, *Trans.*, 1887, 51, 425), or with acetic anhydride and sodium acetate (Japp and Lander, *Trans.*, 1897, 71, 130), it yields the dehydration product, but with acetic anhydride it remains unchanged (Japp and Miller, *Trans.*, 1885, 47, 33). The behaviour of the dehydration product on heating led Japp and Burton to represent the dehydration thus :



The behaviour of the dehydration derivative on heating a little above its melting point agrees almost exactly with the equation :



Japp and Meldrum (*Trans.*, 1901, 79, 1031), by boiling α -methyl-anhydroacetonebenzil with dilute sulphuric acid, or with glacial acetic acid, obtained a dehydration product, $C_{36}H_{28}O_2$, melting and decomposing at 230°. The reaction is represented by the equation :

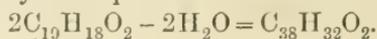


and is analogous to the dehydration of anhydroacetonebenzil. Japp and Meldrum obtained the same dehydration product from β -methyl-anhydroacetonebenzil by the action of anhydrous formic acid, whereas desylenemethyl ethyl ketone, $COPh \cdot CPh \cdot CH \cdot COEt$, was formed by the action of glacial acetic acid.

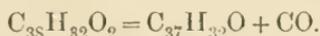
I have prepared these dehydration products by other methods, and have obtained also the dehydration products of $\alpha\beta$ -dimethylanhydroacetonebenzil and benzylidene- α -methylanhydroacetonebenzil, the ethyl ethers of α -methylanhydroacetonebenzil and benzylidene- α -methylanhydroacetonebenzil, and the acetyl derivatives of $\beta\beta$ -dimethylanhydroacetonebenzil and benzylideneanhydroacetonebenzil.

By boiling anhydroacetonebenzil with absolute alcohol and sulphuric acid, or by treating it with cold acetic anhydride and sulphuric acid, the dehydration product is obtained ; cold glacial acetic acid, containing a few drops of concentrated sulphuric acid, leaves the substance unchanged. Acetic anhydride and sulphuric acid effect dehydration of α - and β -methylanhydroacetonebenzil. On boiling α -methyl-anhydroacetonebenzil with ethyl alcohol and sulphuric acid, the ethyl ether is obtained, and when methyl alcohol is used, in this reaction, the methyl ether is formed. β -Methylanhydroacetonebenzil is not attacked when boiled with ethyl alcohol and sulphuric acid, or when treated with cold glacial acetic acid containing a few drops of concentrated sulphuric acid.

Cold acetic anhydride and sulphuric acid, and also cold glacial acetic acid containing a few drops of concentrated sulphuric acid, effect dehydration in $\alpha\beta$ -dimethylanhydroacetonebenzil. The reaction may be represented by the equation :



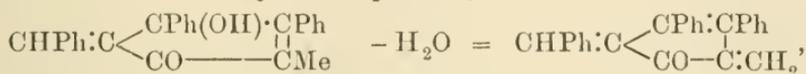
The product melts at 181—182°, and evolves carbon monoxide. The action of heat may, on the analogy of the behaviour of the dehydration product of anhydroacetonebenzil, be represented as



Whilst there are indications that this analogy holds good, yet neither for the dehydration product of α -methylanhydroacetonebenzil nor for that of $\alpha\beta$ -dimethylanhydroacetonebenzil have I obtained exact quantitative results, such as were found in the case of the anhydroacetonebenzil dehydration product.

The dehydration product of benzylidene- α -methylanhydroacetonebenzil is prepared by the action of cold acetic anhydride and sulphuric acid; it melts at 245°, no evolution of gas being observed.

In this case possibly one molecule of the original substance yields one molecule of the dehydration product, thus:



the double linking in the five-carbon ring changing its position, whereas in the case of the four other dehydration products two molecules of the original substance give one molecule of the dehydration product.

By boiling benzylidene- α -methylanhydroacetonebenzil with absolute ethyl alcohol and concentrated sulphuric acid, the ethyl ether is produced.

Thus, whilst the direct evidence of acetylation has not been forthcoming as a proof of the presence of the hydroxyl group in Nos. I, II, III, IV, and VII of the above list, yet in the case of α -methyl- and benzylidene- α -methyl-anhydroacetonebenzil I have succeeded in preparing ethyl ethers by the action of boiling absolute alcohol and sulphuric acid.

It is to be noted that, when the ethyl ether is obtained by this method, the original substance contains a methyl group in the α -position. The same treatment gives in the case of anhydroacetonebenzil the dehydration derivative, and leaves the benzylidene- β -methyl and $\beta\beta$ -dimethyl derivatives unchanged. The action on $\alpha\beta$ -dimethyl- and β -isopropylidene-anhydroacetonebenzil has not been tried.

In this connexion it may be remarked that the same treatment yields an ethyl derivative in the case of α -methylanhydroacetone-dibenzil (Japp and Meldrum, *loc. cit.*, p. 1035). This agrees with the above rule, to which there is no exception.

The ethyl ether of α -methylanhydroacetonebenzil (m. p. 110°) yields on reduction with concentrated hydriodic acid, 3:4-diphenyl-2-methyl- Δ^3 -cyclopentenone, already obtained by Japp and Meldrum

(*loc. cit.*) by the reduction of α -methyl-anhydroacetonebenzil; again the ethyl ether of α -methyl-anhydroacetonebenzil yields α -methyl-anhydroacetonebenzil on oxidation with hydrogen peroxide, and a benzylidene derivative when treated with benzaldehyde and alcoholic potash. This derivative is also produced by the action of boiling absolute alcohol, containing a few drops of concentrated sulphuric acid, on benzylidene- α -methyl-anhydroacetonebenzil, as was to be expected.

Its formation from the ethyl ether of α -methyl-anhydroacetonebenzil is to be taken as a proof of the presence of the group $\text{CH}_2\cdot\text{CO}$ in the latter. Wallach and others have shown that the condensation of aldehydes with cyclic ketones takes place only when the latter contain a methylene group directly attached to carbonyl.

EXPERIMENTAL.

Dehydration Product of $\alpha\beta$ -Dimethyl-anhydroacetonebenzil, $\text{C}_{38}\text{H}_{32}\text{O}_2$.

Five grams of $\alpha\beta$ -dimethyl-anhydroacetonebenzil, 20 c.c. of acetic anhydride, and 10 drops of concentrated sulphuric acid were mixed at the ordinary temperature. The liquid became green, and crystals quickly separated out (3.8 grams). On recrystallisation from hot alcohol, long, rectangular prisms were obtained, melting and decomposing at $181\text{--}182^\circ$:

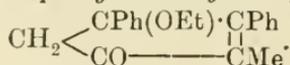
0.1495 gave 0.4807 CO_2 and 0.0832 H_2O . $\text{C} = 87.66$; $\text{H} = 6.18$.*

$\text{C}_{38}\text{H}_{32}\text{O}_2$ requires $\text{C} = 87.69$; $\text{H} = 6.15$ per cent.

Analogous dehydration products have already been prepared by other experimenters, and new methods of preparing these substances have been discovered in the present research, as explained above.

Of these, the simplest is that in which acetic anhydride and sulphuric acid are employed, the preparation being analogous to that just described, except that in the other cases the product is not obtained in so short a time. A very minute proportion of concentrated sulphuric acid is effective.

4-Ethoxy-3 : 4-diphenyl-2-methyl- Δ^2 -cyclopentenone,



A mixture of 3 grams of α -methyl-anhydroacetonebenzil, 60 c.c. of absolute ethyl alcohol, and 3 drops of concentrated sulphuric acid was boiled for three hours. Water precipitated a solid, which crystal-

* At least two analyses were made in the great majority of cases in this and the following paper, but only one analysis is given here as elsewhere in order to save space.

lised from its hot alcoholic solution in lustrous laminæ melting at 110°:

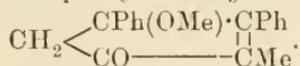
0.1504 gave 0.4537 CO₂ and 0.0953 H₂O. C = 82.27; H = 7.05.

C₂₀H₂₀O₂ requires C = 82.19; H = 6.85 per cent.

Action of Hydrogen Peroxide.—When a mixture of 3 grams of this substance, with sufficient glacial acid to dissolve it, and 200 c.c. of hydrogen peroxide (6 per cent.) was heated on the water-bath for four hours, *α*-methyl-anhydroacetonebenzil was obtained in good yield.

Action of Hydriodic Acid.—A mixture of 2 grams of 4-ethoxy-3:4-diphenyl-2-methyl- Δ^2 -cyclopentenone and 20 grams of concentrated hydriodic acid (D 1.96) was boiled for four minutes. After adding water, the precipitate was extracted with ether, the ethereal solution shaken with sulphurous acid and then with sodium carbonate solution, and dried. On spontaneous evaporation, pale yellow, six-sided, oblique, flat prisms or plates separated, which, when recrystallised from light petroleum, melted at 77—78°, and were proved to consist of 3:4-diphenyl-2-methyl- Δ^3 -cyclopentenone.

4-Methoxy-3:4-diphenyl-2-methyl- Δ^2 -cyclopentenone,

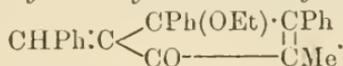


The preparation of this substance is similar to that of the corresponding ethyl ether. It crystallised from alcohol in small, rectangular plates melting at 69°:

0.1650 gave 0.4959 CO₂ and 0.0983 H₂O. C = 81.96; H = 6.62.

C₁₉H₁₈O₂ requires C = 82.01; H = 6.47 per cent.

4-Ethoxy-3:4-diphenyl-5-benzylidene-2-methyl- Δ^2 -cyclopentenone,



This substance was prepared by two methods:

(1) Two grams of 4-ethoxy-3:4-diphenyl-2-methyl- Δ^2 -cyclopentenone were dissolved in alcoholic potash (3 grams of potassium hydroxide in 50 grams of absolute alcohol), and 1 gram of benzaldehyde was added, the mixture being kept at the ordinary temperature for twenty-four hours. The crystals which separated, after recrystallisation from hot alcohol, contained alcohol of crystallisation, and melted at 149.5°. When crystallised from light petroleum, they separated in long, six- or eight-sided plates, melting at 150°. The total yield was about 2 grams. After being kept overnight in a vacuum over sulphuric acid, the substance crystallised from alcohol was analysed:

0.1652 gave 0.5025 CO₂ and 0.1004 H₂O. C = 82.94; H = 6.75.

0.2439, heated at 120°, lost 0.0110. EtOH = 4.59.

2C₂₇H₂₄O₂, EtOH requires C = 83.37; H = 6.70; EtOH = 4.57 per cent.

After being kept in a vacuum over sulphuric acid for several days:

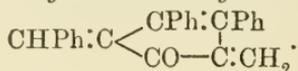
0.1560 gave 0.4831 CO₂ and 0.0928 H₂O. C = 84.45; H = 6.61.

C₂₇H₂₄O₂ requires C = 85.20; H = 6.31 per cent.

The substance had therefore not completely parted with its alcohol. A specimen freed from its alcohol by heating has not yet been analysed. It seems likely, however, that the above formula would be confirmed.

(2) A mixture of benzylidene- α -methyl-anhydroacetonebenzil, ethyl alcohol, and concentrated sulphuric acid was boiled for several hours, and the product recrystallised from alcohol. The first crop of crystals consisted of unchanged substance. The crystals from the mother liquor were treated with three successive portions of boiling light petroleum, when the second and third portions gave unchanged substance, but from the first extract there were deposited pale yellow, six- or eight-sided plates and a small amount of minute, white crystals. These, being specifically lighter, were separated from the heavier, yellow crystals by means of hot light petroleum. The latter crystals, of which the yield was poor, were identified by the mixed melting-point test as 4-ethoxy-3:4-diphenyl-5-benzylidene-2-methyl- Δ^2 -cyclopentenone.

3:4-Diphenyl-5-benzylidene-2-methylene- Δ^3 -cyclopentenone,

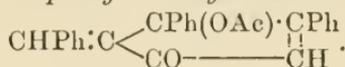


This substance was prepared as follows:

Ten grams of benzylidene- α -methyl-anhydroacetonebenzil, 60 gramms of acetic anhydride, and 6 drops of concentrated sulphuric acid were kept at the ordinary temperature for four days, and the red solid which had precipitated was washed with alcohol. After crystallisation from benzene and light petroleum, and then from benzene and alcohol, 2 grams of a yellow substance, melting at 245°, were obtained. This was insoluble in alcohol, and very soluble in benzene:

0.1454 gave 0.4746 CO₂ and 0.0710 H₂O. C = 89.00; H = 5.42.

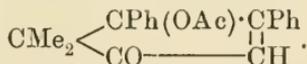
C₂₅H₁₈O requires C = 89.8; H = 5.4 per cent.

4-Acetoxy-3 : 4-diphenyl-5-benzylidene- Δ^2 -cyclopentenone,

Sixteen grams of benzylideneanhydroacetonebenzil (m. p. 232°), 128 c.c. of acetic anhydride, and 16 drops of concentrated sulphuric acid were mixed, and kept at the ordinary temperature for twenty-four hours. More than this amount of sulphuric acid was found to blacken the mixture. The solid which precipitated was separated by filtration, washed with cold alcohol, and extracted with successive portions of boiling alcohol, from which it crystallised in very slender, yellow needles, melting at 175° . The yield was 8 grams. The same substance was obtained in a similar experiment performed with the modification of benzylideneanhydroacetonebenzil, melting at 213.5° (see following paper):

0.1354 gave 0.4078 CO_2 and 0.0659 H_2O . C = 82.14; H = 5.40.

$\text{C}_{26}\text{H}_{20}\text{O}_3$ requires C = 82.10; H = 5.26 per cent.

4-Acetoxy-3 : 4-diphenyl-5 : 5-dimethyl- Δ^2 -cyclopentenone,

As a large amount of this product was required for experiments on its hydrolysis (see following paper), the method of employing a mixture of acetic anhydride and sulphuric acid at the ordinary temperature was varied by reducing the quantity of anhydride and acid, whereby the yield of acetyl derivative was improved: 72 grams of $\beta\beta$ -dimethylanhydroacetonebenzil, 120 grams of acetic anhydride, and 15 drops of sulphuric acid were heated on a sand-bath until all the solid had dissolved; on cooling, large, stout, oblique, four-sided plates separated, which, when recrystallised from alcohol, melted at 137° . The yield was 77 grams:

0.1448 gave 0.4157 CO_2 and 0.0843 H_2O . C = 78.30; H = 6.47.

$\text{C}_{21}\text{H}_{20}\text{O}_3$ requires C = 78.75; H = 6.25 per cent.

A negative result was obtained with glacial acetic acid and concentrated sulphuric acid.

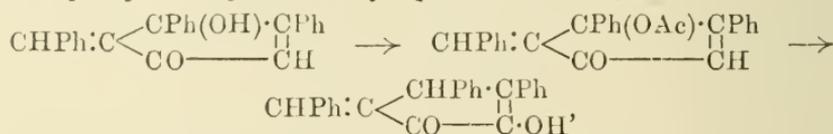
CCXXX.—*Isomerides of Anhydroacetonebenzil and its Derivatives.*

By FRANCIS WILLIAM GRAY.

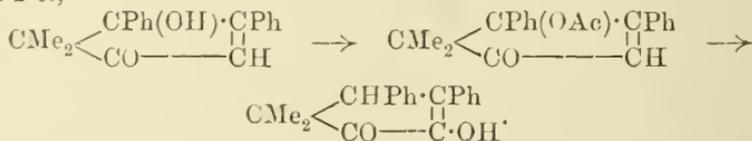
By treating the acetyl derivatives of benzylideneanhydroacetonebenzil and $\beta\beta$ -dimethylanhydroacetonebenzil (see preceding paper) with alcoholic potash, substances were obtained isomeric with the parent compounds, but differing from these in physical and chemical behaviour. The products of deacetylation are soluble in aqueous potassium hydroxide, and are precipitated from the solution with carbon dioxide, thus behaving like monohydric phenols; they also give the ferric chloride colour test characteristic of these compounds.

Japp and Knox treated the acetyl derivative of β -isopropylideneanhydroacetonebenzil in the same way with alcoholic potash. The resulting substance was not isolated in the pure state, but it showed no sign of dissolving in aqueous potassium hydroxide, and I found that it did not give a coloration with ferric chloride, so that the deacetylation in this case does not seem to proceed in the same way as do the deacetylations already mentioned.

In the two cases mentioned above, where deacetylation leads to new phenolic compounds, the constitution of the latter has been investigated, and it has been found that benzylideneanhydroacetonebenzil (3 : 4-diphenyl-5-benzylidene- Δ^2 -cyclopenten-1-one-4-ol) yields 3 : 4-diphenyl-5-benzylidene- Δ^2 -cyclopenten-1-one-2-ol,



and $\beta\beta$ -dimethylanhydroacetonebenzil (3 : 4-diphenyl-5 : 5-dimethyl- Δ^2 -cyclopenten-1-one-4-ol) gives 3 : 4-diphenyl-5 : 5-dimethyl- Δ^2 -cyclopenten-1-one-2-ol,

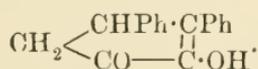


On deacetylation of their acetyl derivatives (prepared by means of acetic anhydride and sulphuric acid), the 2-hydroxy-compounds are regenerated.

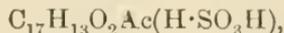
When the results obtained with boiling acetic anhydride alone as an acetylating agent are considered, there are introduced in the case of the first substance, possibilities which make the changes more complicated than the above. This will be explained later.

Thus, in the present research, 2-hydroxy-compounds have been obtained isomeric with two of the eight 4-hydroxy-compounds mentioned in the list given at the beginning of the preceding paper. In the case of one of the three 4-hydroxy-compounds which give acetyl derivatives, hydrolysis does not yield a 2-hydroxy-isomeride, so that in the case of the five substances from which acetyl derivatives have not been prepared, the method of the present research might not lead to 2-hydroxy-isomerides even if acetyl derivatives or other esters should be prepared, and even if the 2-position in the five-carbon ring is occupied by the hydrogen atom. But other methods may be available. In fact, the 2-hydroxy-isomeride of anhydroacetonebenzil itself has been prepared by Vorländer and Schroedter (*Ber.*, 1903, **36**, 1490; compare also Vorländer and von Liebig, *Ber.*, 1904, **37**, 1133; von Liebig, *Diss.*, Halle, 1904; and Metge, *Diss.*, Halle, 1904).

Vorländer and Schroedter, by acting with acetic anhydride and a large quantity of concentrated sulphuric acid on dibenzylideneacetone, obtained a substance, $C_{17}H_{13}O_2Ac(H \cdot SO_3H)$, from which, on hydrolysis, was obtained a compound, $C_{17}H_{14}O_2$, to which they assigned the constitution:



The constitution of the intermediate compound, $C_{17}H_{13}O_2Ac(H \cdot SO_3H)$ has not been ascertained, but the fact that the final reduction product of the 2-hydroxy-compound (namely, the hydrocarbon, $C_{17}H_{18}$ or $\begin{array}{l} \text{CHPh} \cdot \text{CH}_2 \\ | \\ \text{CHPh} \cdot \text{CH}_2 \end{array} > \text{CH}_2$) is obtained from the sulphurous acid compound, from the 2-hydroxy-compound, and from the intermediate reduction product of the 2-hydroxy-compound (namely, from the ketone, $C_{17}H_{16}O$, $\begin{array}{l} \text{CHPh} \cdot \text{CH}_2 \\ | \\ \text{CHPh} - \text{CO} \end{array} > \text{CH}_2$, or $\begin{array}{l} \text{CHPh} \cdot \text{CH}_2 \\ | \\ \text{CHPh} \cdot \text{CH}_2 \end{array} > \text{CO}$) by reduction with hydriodic acid, is given as evidence in support of the theory that the five-carbon ring is present in the intermediate compound,

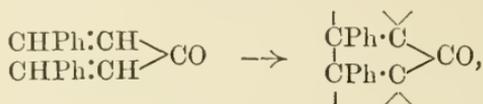


and against the theory that the closing of the five-carbon ring takes place on hydrolysis. It cannot be maintained, however, that the position in the ring occupied by the acetoxy-group is the same as that occupied by the hydroxyl group of the 2-hydroxy-compound obtained on hydrolysis. Further, in the light of the results here described, it seems possible that the first hydroxyl group may occupy the 4-position. Thus, the method of preparing the acetyl derivative of the 2-hydroxy-compound, and then treating it with sodium hydrogen sulphite, the method adopted by Metge in attempting unsuccessfully to synthesise the compound, $C_{17}H_{13}O_2Ac(H \cdot SO_3H)$, even

if it gave a substance of the desired percentage composition, might lead to one of different constitution.

In defence of the constitution given above for the substance $C_{17}H_{14}O_2$, Vorländer quotes the following experimental results :

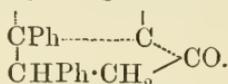
Boiling with concentrated aqueous potassium hydroxide gave deoxybenzoin and monomethylstilbene, $C_6H_5 \cdot CMe : CH \cdot C_6H_5$, showing that the following change had occurred :



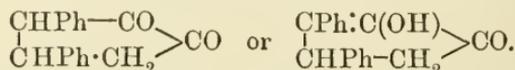
the two β -carbon atoms of dibenzylideneacetone uniting, and the five-carbon ring being formed.

Oxidation with chromic acid or with permanganate gave benzil and desylacetic acid, $\text{CPhBz} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$.

This, and the fact that a benzylidene derivative was formed by condensation with benzaldehyde, agree with the structure :



As far as these results are concerned, the constitution might be



No sign of a quinoxaline derivative has been observed on treatment with *o*-phenylenediamine, so that the former formula is improbable. The latter is therefore chosen ; and this is confirmed by the acid properties of the substance, and the formation of acetyl and benzoyl derivatives.

The benzylidene derivative of Vorländer's 2-hydroxy-compound, referred to above, is of considerable importance in connexion with the present research. Before knowing that von Liebig had prepared this derivative, it occurred to the author that it might be of interest to prepare this substance from Vorländer's 2-hydroxy-compound and to compare it with the 2-hydroxy-isomeride of benzylideneanhydroacetonebenzil, obtained by the method described in the present paper. It was to be expected that these two benzylidene compounds would be identical.

The benzylidene-2-hydroxy-compound prepared, for comparison, by Vorländer's method had the correct percentage composition, $C_{24}H_{18}O_2$, and agreed with the description given by von Liebig, crystallising in fine, yellow needles (m. p. 223°).

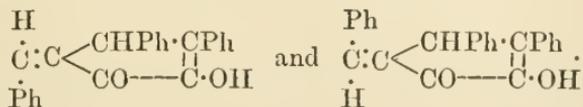
The benzylidene-2-hydroxy-compound obtained from benzylideneanhydroacetonebenzil had the same appearance, but melted at 216°.

These two compounds are chemical isomerides. This is not a case of dimorphism, but, perhaps, of maleoid and fumaroid isomerism.

The two substances give the same dark brown coloration with ferric chloride, and they yield, on acetylation in the cold with acetic anhydride and sulphuric acid, the same acetyl derivative (yellow needles, m. p. 175—176°), from which, on deacetylation, the 2-hydroxy-compound, melting at 216°, is obtained. It should be noted, however, that in this acetylation of the 2-hydroxy-compound melting at 216°, a very small quantity of another substance (acetyl derivative) is obtained, crystallising in almost colourless plates, melting at 148—152° (softening at 148°).

Again, these 2-hydroxy-compounds, when boiled with acetic anhydride alone, both give the same acetyl derivative, crystallising in almost colourless plates, melting at 148—152° (according to von Liebig, almost colourless, oblique prisms, m. p. 148—149°), which was shown by the mixed melting-point test to be the same as the substance obtained in small quantity by acetylation with acetic anhydride and sulphuric acid. The acetyl derivative melting at 148—152° yields, on deacetylation, the 2-hydroxy-compound melting at 223°.

The direct transformation of the more soluble and less stable 2-hydroxy-compound, melting at 216°, into the less soluble and more stable 2-hydroxy-compound, melting at 223°, can be effected by means of a concentrated solution of hydrogen chloride in absolute alcohol. The 2-hydroxy-compounds may have the configurations :



No experimental results, however, are available for settling which of these configurations is to be assigned to the more stable substance, nor are there even, so far as the author is aware, any analogies which might serve as a guide in arriving at a conclusion.

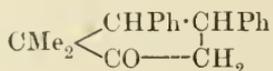
Experiments carried out with the 2-hydroxy-isomeride of $\beta\beta$ -dimethylanhydroacetonebenzil, $\text{C}_{19}\text{H}_{18}\text{O}_2$ (m. p. 155—156°), lead to a constitution similar to that given by Vorländer to the 2-hydroxy-isomeride of anhydroacetonebenzil :

(1) Oximation experiments were successful in the case of $\beta\beta$ -dimethylanhydroacetonebenzil and its acetyl derivative, but failed in the case of the 2-hydroxy-compound, with which hydroxylamine seems to react, giving two substances, of which the amounts obtained were too small for analysis. A phenylhydrazone, however, is obtained with the 2-hydroxy-compound. These results show the presence of one carbonyl group in each of the substances examined.

(2) A methyl ether, $\text{C}_{19}\text{H}_{17}\text{O}(\text{OMe})$ (m. p. 88·5°), and an acetyl derivative, $\text{C}_{19}\text{H}_{17}\text{O}(\text{OAc})$ (m. p. 92·5°), were obtained.

(3) Reduction of the 2-hydroxy-compound with hydriodic acid

yields a neutral substance, $C_{19}H_{20}O$ (m. p. 153°), which reacts with hydroxylamine; to this substance the formula

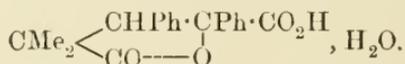


may be assigned.

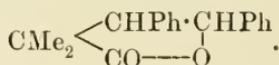
$\beta\beta$ -Dimethylanhydroacetonebenzil should, on reduction, yield the same product, but no definite substance could be isolated from this reaction.

(4) Oxidation with permanganate or with hydrogen peroxide gives α -desylisobutyric acid, $COPh \cdot CHPh \cdot CMe_2 \cdot CO_2H$.

(5) Oxidation with potassium hypobromite gives an acid, $C_{19}H_{20}O_5$ (m. p. 197°), to which the following constitution has been assigned :



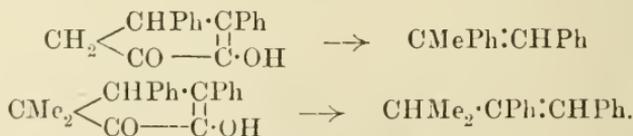
This structure agrees with the following properties of this acid : (a) It loses a molecule of water at 113° . (b) It is inert towards acetylating agents. (c) It is inert towards hydriodic acid unless the mixture is heated with red phosphorus in a sealed tube at 150° , when it yields $\beta\gamma$ -diphenyl- $\alpha\alpha$ -dimethylbutyric acid, $CH_2Ph \cdot CHPh \cdot CMe_2 \cdot CO_2H$, and the lactone of γ -hydroxy- $\beta\gamma$ -diphenyl- $\alpha\alpha$ -dimethylbutyric acid,



(d) It is a monobasic acid, as shown by the analysis of its silver salt and by titration with standard alkali.

(e) It is a lactone of the acid $CO_2H \cdot CPh(OH) \cdot CHPh \cdot CMe_2 \cdot CO_2H$, the disodium salt of which has been prepared from the acid $C_{19}H_{20}O_5$, the lactone ring being broken in the process.

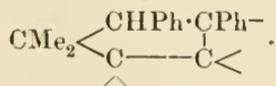
(6) The experiments with potassium hydroxide were of considerable importance in the case of Vorländer's 2-hydroxy-compound, showing, as they did, that the two β -carbon atoms of dibenzylideneacetone had united, the five-carbon ring being formed. Now, although the same experiment does not throw the same light on the constitution of the 2-hydroxy-isomeride of $\beta\beta$ -dimethylanhydroacetonebenzil (the benzil residue being already present in $\beta\beta$ -dimethylanhydroacetonebenzil), it seemed likely that the product obtained would be *isopropylstilbene* on the analogy of Vorländer's experiment which gives monomethylstilbene, thus :



The product, however, was stilbene itself. This result is not to be

regarded as inconsistent with the constitution indicated by the other experiments described in this paper.

The oxidation experiments and the empirical formula show that the structure of the 2-hydroxy-compound must be



Acetylation and methylation experiments show that the substance contains a hydroxyl group, and the action of phenylhydrazine proves the presence of a carbonyl group; consequently, the only way of accounting for these is by the expression



This formula is consistent, not only with the chemical properties of the substance itself, but also with the results obtained by Vorländer in his experiments on the 2-hydroxy-isomeride of anhydroacetonebenzil.

EXPERIMENTAL.

Benzylideneanhydroacetonebenzil.

On repeating Japp and Findlay's method of preparation of this substance (*Trans.*, 1899, **75**, 1023), there was found in the first hot alcoholic extract of the crude product (which Japp and Findlay assumed to give unchanged anhydroacetonebenzil) a substance crystallising in prisms, melting at 213.5°. Subsequent extracts yielded six-sided plates (m. p. 232°).

The substance melting at 213.5° was found to be isomeric with benzylideneanhydroacetonebenzil :

0.1472 gave 0.4582 CO₂ and 0.0740 H₂O. C = 84.96 ; H = 5.59.

C₂₄H₁₈O₂ requires C = 85.20 ; H = 5.32 per cent.

The substance melting at 232° had the appearance and melting point hitherto assigned to benzylideneanhydroacetonebenzil.

When treated with acetic anhydride and concentrated sulphuric acid, these two substances give the same acetyl derivative, melting at 175° (see preceding paper). They are different forms of benzylideneanhydroacetonebenzil, perhaps maleoid and fumaroid isomerides.

Japp and Findlay found (*Trans.*, 1899, **75**, 1018) that acetic anhydride alone did not act on benzylideneanhydroacetonebenzil (m. p. 232°) even when the temperature was raised to 150°; this is of

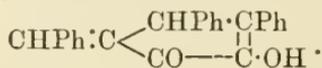
* The substance is not only an enol, but also a ketone *at the same time*, and Vorländer uses the term "keto-enol" in referring to a compound of this kind. This name has, however, been rejected by the present author, because in what is usually called "keto-enolic isomerism" the substance is an enol and a ketone *alternately*.

interest in connexion with the behaviour of the two 2-hydroxy-isomerides.

The yield of the substance melting at 213·5° was small, whilst about 24 grams of the substance melting at 232° were obtained from 20 grams of anhydroacetonebenzil.

An attempt to transform from the one substance to the other was not successful. There are indications, however, that the substance melting at 213·5° can be converted into the substance melting at 232° by means of an alcoholic solution of hydrogen chloride.

3 : 4-Diphenyl-5-benzylidene- Δ^2 -cyclopenten-1-one-2-ol (m. p. 216°),



Eight grams of the acetyl derivative (m. p. 175°) of benzylidene-anhydroacetonebenzil were mixed with an excess of a 5 per cent. alcoholic solution of potassium hydroxide. The acetyl derivative dissolved, giving a red solution, and much heat was developed. This solution was kept at the ordinary temperature for a few days. If water is added to the red liquid, a brilliant red solid is obtained, but if the red liquid is acidified with hydrochloric acid, the red colour disappears and a yellow precipitate is formed. This dissolves in aqueous potassium hydroxide, from which it is reprecipitated by carbon dioxide. Its alcoholic solution gives with a drop of ferric chloride solution a dark brown coloration.

The substance crystallises from alcohol in small clusters of fine needles melting at 216° :

0·1646 gave 0·5157 CO₂ and 0·0794 H₂O. C = 85·45 ; H = 5·36.

C₂₄H₁₈O₂ requires C = 85·20 ; H = 5·32 per cent.

3 : 4-Diphenyl-5-benzylidene- Δ^2 -cyclopenten-1-one-2-ol (m. p. 223°).

3 : 4-Diphenyl- Δ^2 -cyclopenten-1-one-2-ol was prepared by the method described by Vorländer (*loc. cit.*) ; the following points require special attention.

During the gradual addition of sulphuric acid, the temperature should not be allowed to fall lower than 25—30°, the temperature recommended by Vorländer.

After the addition of all the acid, too long a time should not elapse before the mixture is worked up. The whole preparation should be carried out in one day. Further, in heating with alkali to effect hydrolysis of the intermediate sulphurous acid compound, sufficient time should be given for the reaction to be completed, otherwise, on acidifying, there will be obtained a product difficult to purify.

One gram of 3 : 4-diphenyl- Δ^2 -cyclopenten-1-one-2-ol was dissolved in 30 c.c. of absolute alcohol containing 1 gram of potassium hydroxide, and 0.5 gram of benzaldehyde was added. This mixture was kept at the ordinary temperature for four days. On adding it to a large bulk of water, a clear solution was obtained, and, on passing carbon dioxide through it, an orange-coloured precipitate was obtained, which crystallised from hot alcohol in clusters of light yellow needles melting at 220°. Von Liebig gives the melting point 223—224°, and by employing another method of preparing this substance, the present author obtained it with the melting point 223°. The product is therefore probably identical with von Liebig's compound, although the melting points differ slightly. The yield of pure substance recrystallised from alcohol was 0.55 gram :

0.1464 gave 0.4560 CO₂ and 0.07 H₂O. C = 84.94 ; H = 5.31.

C₂₄H₁₈O₂ requires C = 85.20 ; H = 5.32 per cent.

This substance is also obtained when the 2-hydroxy-compound melting at 216° is added to enough of a concentrated solution of hydrogen chloride in absolute alcohol to give a clear solution ; it crystallises from this solution in a very pure state, and in large amount.

2-Acetoxy-3 : 4-diphenyl-5-benzylidene- Δ^2 -cyclopentenone



When the 2-hydroxy-compound melting at 216° was treated with acetic anhydride and a few drops of sulphuric acid at the ordinary temperature, two products were obtained, the chief of which crystallised from alcohol in very fine needles melting at 175—176°, and retaining their form on recrystallisation. From the alcoholic mother liquor there separated a very small quantity of almost colourless, rhombic plates, the melting point of which was rather indefinite. The substance softened at about 148—149°, and melted to a clear liquid a few degrees higher.

Analysis of the compound melting at 175—176° :

0.0936 gave 0.2795 CO₂ and 0.0468 H₂O. C = 81.43 ; H = 5.55.

C₂₆H₂₀O₃ requires C = 82.10 ; H = 5.26 per cent.

A mixture of the acetyl derivative (m. p. 175°) of benzylidene-anhydroacetonebenzil and the acetyl derivative (m. p. 175—176°) of the 2-hydroxy-compound melted at 155°, showing that these substances, although they have the same composition and melting point, are not identical.

This substance (m. p. 175—176°) may also be prepared by the action

of acetic anhydride and sulphuric acid at the ordinary temperature on the 2-hydroxy-compound melting at 223°.

The hydrolysis of this ester may be effected by means of 5 per cent. alcoholic potash, the method being similar to that employed in the preparation of 3:4-diphenyl-5-benzylidene- Δ^2 -cyclopenten-1-one-2-ol (p. 2144); the 2-hydroxy-compound melting at 216° is obtained.

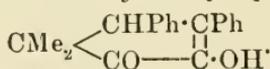
2-Acetoxy-3:4-diphenyl-5-benzylidene- Δ^2 -cyclopentenone
(m. p. 148—152°).

A mixture of 12 grams of acetic anhydride and 0.6 gram of the 2-hydroxy-compound melting at 216° was boiled for one and a-half hours. The product obtained on adding water crystallised from benzene in almost colourless, rhombic plates, which soften at 148—149° and melt to a clear liquid at about 152°. Liebig, by the action of boiling acetic anhydride on the 2-hydroxy-compound melting at 223°, obtained an acetyl derivative which he describes as consisting of almost colourless, oblique prisms melting at 148—149°. These acetyl derivatives are doubtless the same.

On hydrolysis by means of 5 per cent. alcoholic potash, the 2-hydroxy-compound melting at 223° is obtained.

From the hydrolysis experiments, therefore, the acetyl derivative melting at 148—152° corresponds with the 2-hydroxy-compound melting at 223°, and the acetyl derivative melting at 175—176° corresponds with the 2-hydroxy-compound melting at 216°.

3:4-Diphenyl-5:5-dimethyl- Δ^2 -cyclopenten-1-one-2-ol,



Five grams of the acetyl derivative (m. p. 137°) of $\beta\beta$ -dimethyl-anhydroacetonebenzil were added to 50 c.c. of a 5 per cent. alcoholic solution of potassium hydroxide. Where the alkali came in contact with the solid acetyl compound, a bright green colour was observed, which disappeared on shaking. A yellow solution was obtained, which was kept at the ordinary temperature for several days. On acidification, the 2-hydroxy-compound was precipitated, which crystallised from alcohol, in which it is very soluble, in pink needles melting at 155—156°. The yield was 4.2 grams:

0.1481 gave 0.4436 CO_2 and 0.0868 H_2O . C = 81.68; H = 6.51.

$\text{C}_{19}\text{H}_{18}\text{O}_2$ requires C = 82.01; H = 6.47 per cent.

This substance dissolves in aqueous potassium hydroxide, from which it is reprecipitated by carbon dioxide. Its alcoholic solution gives with ferric chloride solution a dark brown coloration.

Boiling for five minutes with concentrated hydriodic acid (D 1.96) gives a small quantity of the same product, but most of the 2-hydroxy-compound remains unchanged:

0.1462 gave 0.4626 CO₂ and 0.1014 H₂O. C = 86.28; H = 7.70.

C₁₉H₂₀O requires C = 86.36; H = 7.57 per cent.

The *oxime* crystallises from alcohol as 4C₁₉H₂₁ON, EtOH. The alcohol of crystallisation is removed at 110°:

0.3620 gave 16.2 c.c. N₂ (moist) at 13° and 769 mm. N = 5.35.

C₁₉H₂₁ON requires N = 5.0 per cent.

α-Desylisobutyric acid, CPh·CHPh·CMe₂·CO₂H.

Nine grams of the 2-hydroxy-compound melting at 155—156° were mixed with 18 grams of potassium permanganate and aqueous potassium hydroxide, and kept at the ordinary temperature. The clear filtrate, on being acidified with hydrochloric acid, gave a precipitate, which was dissolved in ether, and the ethereal solution was shaken with sodium carbonate solution. The sodium carbonate extract gave an acid, which was recrystallised from alcohol, and melted, when rapidly heated, at 218°₈ with evolution of gas:

0.1521 gave 0.4268 CO₂ and 0.0880 H₂O. C = 76.52; H = 6.43.

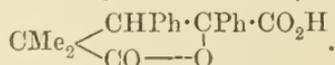
C₁₈H₁₈O₃ requires C = 76.59; H = 6.38 per cent.

Japp and Michie (*Trans.*, 1903, **83**, 309) synthesised *α-desylisobutyric acid* (m. p. 218°), and a mixed melting-point test showed the two acids to be identical.

On treating this acid with acetic anhydride and sulphuric acid at the ordinary temperature, *βγ*-diphenyl-*αα*-dimethyl- Δ^2 -crotonolactone (m. p. 105—106°) was obtained, this being further proof of the identity of the substance (Japp and Michie, *loc. cit.*).

α-Desylisobutyric acid was also obtained by oxidising an alkaline solution of the 2-hydroxy-compound melting at 155—156° with hydrogen peroxide. The product of this oxidation on melting yielded a substance melting at 106°, and the author also found that *α-desylisobutyric acid* decomposed in the same way.

βγ-Diphenyl-αα-dimethylbutyrolactone-γ-carboxylic Acid,



Ten grams of the 2-hydroxy-compound melting at 155—156° were dissolved in a solution of 60 grams of potassium hydroxide in 600 c.c. of water. To this solution was added an alkaline solution of potassium hypobromite, prepared by adding 30 grams of bromine to a solution of 60 grams of potassium hydroxide in 600 c.c. of water. The cold

mixture was kept for two days. A slight precipitate which had formed was then removed, and sulphur dioxide was passed into the cold filtrate. A precipitate was obtained, and the precipitation was completed by acidifying with dilute sulphuric acid. The solid was dissolved in ether, and the ethereal solution was treated with successive portions of an aqueous solution of sodium carbonate and then of an aqueous solution of sodium hydroxide. Practically nothing was obtained in the sodium hydroxide extract. The sodium carbonate yielded an acid which was difficult to purify by recrystallisation from the usual solvents. The method finally adopted was to prepare the pure potassium salt and to acidify its aqueous solution. The acid, further purified by recrystallisation from dilute alcohol, separated in needles melting at 197°.

It is very soluble in alcohol, acetic acid, or benzene, and insoluble in light petroleum. The yield was about 5 grams.

When sodium hypochlorite was used instead of potassium hypobromite, the yield was not improved. Other experiments, in which the proportion of bromine was increased and the temperature raised to that of the water-bath, led to similar results :

0.2014 gave 0.5118 CO₂ and 0.1093 H₂O. C = 69.3 ; H = 6.0.

C₁₉H₂₀O₅ requires C = 69.5 ; H = 6.0 per cent.

The acid crystallises with one molecule of water of crystallisation :

0.3510 lost 0.0190 at 113°. H₂O = 5.4.

C₁₉H₁₈O₄·H₂O requires H₂O = 5.5 per cent.

The crystals effloresce appreciably even under ordinary conditions of temperature and pressure, so that, unless the specimen analysed has been quite recently prepared, the content of water is found too low.

The *silver* salt was prepared :

0.2326 gave 0.0566 Ag. Ag = 24.33.

C₁₉H₁₉O₅Ag requires Ag = 24.82 per cent.

0.4534 of the acid required 7.22 c.c. of alcoholic sodium ethoxide (1 c.c. = 0.00446 gram Na). M.W. (for a monobasic acid) = 324.5.

C₁₉H₂₀O₅ requires M.W. = 328.

The acid is shown below to be a lactone of α -hydroxy- $\alpha\beta$ -diphenyl- $\gamma\gamma$ -dimethylglutaric acid, CO₂H·CPh(OH)·CHPh·CMe₂·CO₂H. The formation of a little of the sodium salt of this dibasic acid before the neutral point is reached may explain the excess of alkali required in the above titration.

The acid is inert towards acetic anhydride containing a few drops of concentrated sulphuric acid, and towards boiling acetic anhydride.

On reduction with hydriodic acid and red phosphorus by heating for

three hours at 150° in a sealed tube, the acid gave $\beta\gamma$ -diphenyl- $\alpha\alpha$ -dimethylbutyric acid, which was obtained by Japp and Michie (Trans., 1903, 83, 311, 312), and also $\beta\gamma$ -diphenyl- $\alpha\alpha$ -dimethylbutyrolactone. Both these products were identified by the mixed melting-point test.

Sodium α -Hydroxy- $\alpha\beta$ -diphenyl- $\gamma\gamma$ -dimethylglutarate,
 $\text{CO}_2\text{Na}\cdot\text{CPh}(\text{OH})\cdot\text{CHPh}\cdot\text{CMe}_2\cdot\text{CO}_2\text{Na}.$

$\beta\gamma$ -Diphenyl- $\alpha\alpha$ -dimethylbutyrolactone- γ -carboxylic acid was dissolved in absolute alcohol, and a solution of sodium ethoxide in absolute alcohol was added in excess of that required for the formation of a dibasic salt. Phenolphthalein indicated the point at which enough sodium ethoxide was added to form the monobasic salt. When excess of twice this quantity of sodium ethoxide solution had been run in, and the solution had been gently heated, a bulky precipitate of the dibasic salt was obtained. The pure white *sodium* salt was collected and washed with absolute alcohol.

The salt crystallises with two molecules of alcohol of crystallisation, which are partly lost in a vacuum over sulphuric acid, and completely at 110°:

0.5820 gave 0.2218 Na_2SO_4 . Na = 12.36.

$\text{C}_{19}\text{H}_{18}\text{O}_5\text{Na}_2$ requires Na = 12.39 per cent.

Enough water must have been present in the "absolute" alcohol for the reaction to take place, as the dibasic salt is formed even if the acid melting at 197° is free from water of crystallisation before use in this experiment.

Action of Potassium Hydroxide on 3:4-Diphenyl-5:5-dimethyl- Δ^2 -cyclopenten-1-one-2-ol.

Stilbene, identified by analysis, by the mixed melting-point test, and by the preparation and analysis of the dibromo-derivative, was obtained by boiling the 2-hydroxy-compound melting at 155—156° with 50 per cent. aqueous potassium hydroxide. A small quantity of a substance melting at 157° was also obtained.

The experiment was repeated with various percentages of the alkali; with all the concentrations used (from 15 per cent. upwards), a little of the substance melting at 157° was isolated; with the lower concentrations, the main bulk of the 2-hydroxy-compound was unchanged, and no stilbene was formed; with the higher concentrations, stilbene was obtained, and the yield improved as the alkali concentration increased.

The research of this and the preceding paper was suggested by Prof. Japp, and the author wishes to thank him for the interest he has always taken in the work.

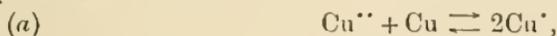
The author also acknowledges the assistance rendered by the Executive Committee of the Carnegie Trust for Scotland, who gave a grant towards expenses.

CHEMICAL DEPARTMENT,
UNIVERSITY OF ABERDEEN.

CCXXXI.—*The Electromotive Behaviour of Cuprous Oxide and Cupric Hydroxide in Alkaline Electrolytes.*

BY ARTHUR JOHN ALLMAND.

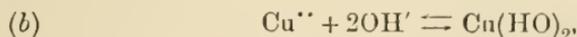
THE object of starting this work was the determination of the solubility product of crystalline cupric hydroxide, a constant of importance in working out the chemistry of the basic salts of copper. The *E.M.F.* of the combination $\text{Cu} \left| \text{Cu}(\text{HO})_2 \text{ alkali} \right| \begin{matrix} \text{Pt} \\ \text{H}_2 \end{matrix}$ was to be measured, and hence the Cu^{++} ion concentration deduced, and the solubility product calculated in the ordinary way. On making measurements, however, it was found that this combination gave values which varied very considerably from hour to hour—which could, in fact, at no time be reproduced with certainty. On consideration, this was recognised to be due to the essential instability of the positive electrode owing to the occurrence of the reaction $\text{Cu}^{++} + \text{Cu} \rightarrow 2\text{Cu}^+$. The following equilibria are involved:



giving the relation

$$\frac{[\text{Cu}^+]^2}{[\text{Cu}^{++}]} = K,$$

and



with the relation $[\text{Cu}^{++}] \cdot [\text{OH}']^2 = k_i$, where k_i is the solubility product of cupric hydroxide.

If we multiply together the above two equations, we get $[\text{Cu}^+]^2 \cdot [\text{OH}']^2 = k_i K$, and hence $[\text{Cu}^+] \cdot [\text{OH}'] = \sqrt{k_i K}$.

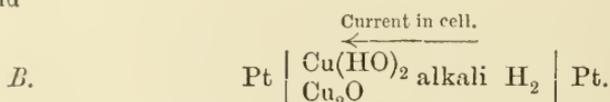
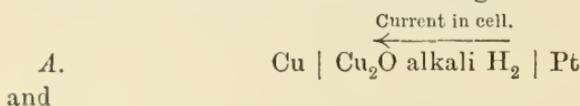
Let $[\text{Cu}^+] \cdot [\text{OH}'] = k_o$ in a saturated solution of cuprous oxide, where k_o is the solubility product of cuprous hydroxide (cuprous oxide).

Then in the present system if $\sqrt{k_i K}$ is greater than k_o , the cupric hydroxide (solid phase) will disappear and form cuprous oxide at the

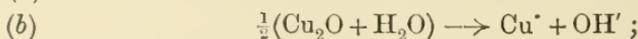
expense of the electrode copper. That this actually is the case can easily be shown experimentally. If a mixture of cupric hydroxide and excess of finely divided copper is shaken up vigorously in a closed vessel with sodium hydroxide solution, the cupric hydroxide will in a few days be completely reduced to cuprous oxide. Now, when cuprous oxide is once precipitated, we have a system with four components (say, copper, oxygen, water, alkali), and with five phases (copper, cuprous oxide, cupric hydroxide, solution, vapour), a system, that is, with one degree of freedom. At a definite alkali concentration, this can only exist in equilibrium at one definite temperature. At any other temperature the potential difference $\text{Cu} \mid \text{Cu}(\text{HO})_2$ alkali will depend on the relative velocities of the reaction $\text{Cu}^{++} + \text{Cu} \rightarrow 2\text{Cu}^+$ and the deposition of cuprous oxide, on the one hand, and of solution of cupric hydroxide, on the other.

Although an electromotive combination involving the reaction $\text{Cu}^{++} \rightarrow \text{Cu} + 2\oplus$ is, in general, unstable in alkaline solution, combinations depending on the reaction $\text{Cu}^+ \rightarrow \text{Cu} + \oplus$, or the reaction $\text{Cu}^{++} \rightarrow \text{Cu}^+ + \oplus$, are stable.

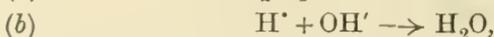
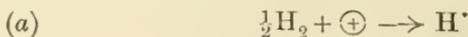
Two such elements are the following :



In combination A, the cathodic reaction for the passage of 96540 coulombs is briefly :



the anodic reaction is :



or, summing up, for the passage of two faradays the total result is $\text{Cu}_2\text{O} + \text{H}_2 \rightarrow 2\text{Cu} + \text{H}_2\text{O}$.

The *E.M.F.* may be expressed as follows.

At the cathode :

$$E_{\text{Cu}^+ \rightarrow \text{Cu}} = (E.P.)_{\text{Cu}^+ \rightarrow \text{Cu}} + 0.058 \log [\text{Cu}^+] \\ = 0.454 + 0.058 \log k_o - 0.058 \log [\text{OH}']$$

where k_o , as before, is the solubility product of cuprous hydroxide.

At the anode :

$$E_{\text{H}' \rightarrow \text{H}} = (E.P.)_{\text{H}' \rightarrow \text{H}} + 0.058 \log [\text{H}'] \\ = 0 + 0.058 \log k_w - 0.058 \log [\text{OH}']$$

where k_w is the dissociation constant of water at the temperature in question.

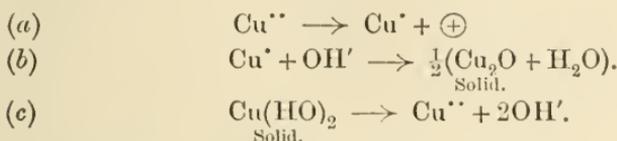
The total *E.M.F.* is hence :

$$E_{\text{Cu}^+ \rightarrow \text{Cu} - \text{E}_{\text{H}^+ \rightarrow \text{H}}} = 0.454 + 0.058 \log \frac{k_o}{k_w} \quad (1).$$

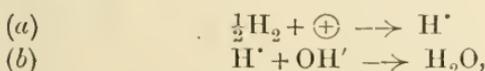
From this, k_o can be calculated.

In combination *B*, the following are the electrode reactions for the passing through of one faraday.

At cathode :



At anode :



or, in the cell, for the passage of two faradays the total result is :



The corresponding *E.M.F.*'s are :

$$\begin{aligned} E_{\text{Cu}^{++} \rightarrow \text{Cu}^+} \text{ At cathode.} &= (\text{E.P.})_{\text{Cu}^{++} \rightarrow \text{Cu}^+} \rightarrow \text{Cu}^+ + 0.058 \log \frac{[\text{Cu}^{++}]}{[\text{Cu}^+]} \\ &= 0.204 + 0.058 \log \frac{k_i}{k_o} - 0.058 \log [\text{OH}']. \end{aligned}$$

$$\begin{aligned} E_{\text{H}^+ \rightarrow \text{H}} \text{ At anode.} &= (\text{E.P.})_{\text{H}^+ \rightarrow \text{H}} \rightarrow \text{H} + 0.058 \log [\text{H}^+]. \\ &= 0 + 0.058 \log k_w - 0.058 \log [\text{OH}']. \end{aligned}$$

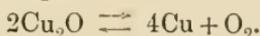
That is,

$$\begin{aligned} \text{E.M.F. of cell} &= E_{\text{Cu}^{++} \rightarrow \text{Cu}^+} - E_{\text{H}^+ \rightarrow \text{H}} \\ &= 0.204 + 0.058 \log \frac{k_i}{k_o \cdot k_w} \quad (2); \end{aligned}$$

k_i is here, as before, the solubility product of cupric hydroxide, and can be calculated, using the value of k_o obtained from equation (1).

Two remarks apply to the above elements. Firstly, it should be noted that the *E.M.F.* is independent of the alkali concentration, always supposing it does not become sufficiently great appreciably to alter the value of k_w , the dissociation constant of water.

Secondly, the first cell may be regarded as an $\text{H}_2\text{-O}_2$ cell, in which hydrogen combines at atmospheric pressure with oxygen supplied at the dissociation pressure at 17° of the reaction :



Before proceeding to the experimental part of the paper, a few additional remarks are necessary. Firstly, it will be noticed that

potential differences (as in the above considerations) are referred to the scale $H_2 | N-H^+ = 0$. Also, that the potential of any single electrode is taken as the potential of electrode minus potential of solution. Secondly, the above calculations presuppose our knowledge of the values $(E.P.)_{Cu^{++} \rightarrow Cu}$ and $(E.P.)_{Cu^+ \rightarrow Cu}$. The latter value was obtained by Bodländer and Storbeck (*Zeitsch. anorg. Chem.*, 1902, 31, 1, 458) in the course of their work on the cuprous salts, as the result of a long series of complex measurements and deductions. The first value is easily calculable by Luther's Law. A redetermination of $(E.P.)_{Cu^+ \rightarrow Cu}$ from fresh and independent data would be of importance. It might perhaps be thought that if the unstable cell $Cu | Cu(OH)_2$ alkali $H_2 | Pt$ were stable, and its *E.M.F.* could be determined, then we should have a third separate equation by means of which this third unknown could be calculated. But even if the combination were stable and measurable, we should not have a third independent equation, for the *E.M.F.* in question ($\pi = 0.329 + 0.029 \log k_i - 0.058 \log k_w$) can readily be calculated from the *E.M.F.*'s of the cells already dealt with. Such a determination, even if practicable, would thus merely confirm or otherwise the *E.M.F.* values for the other two elements.

EXPERIMENTAL.

Two different alkalis, namely, sodium hydroxide and potassium hydroxide, were used. Both were free from carbonate and were prepared from metal. It was afterwards shown that small quantities of carbonate made no final appreciable difference to the potential values. The cupric hydroxide used was crystalline. Colloidal material might be expected to give indefinite results (compare Dawson, this vol., p. 370), apart from the gradual dehydration which would occur in presence of alkali. Preparations were made according to the methods of Becquerel (*Compt. rend.*, 1852, 34, 573) and Böttger (*Jahresb.*, 1858, 198), which are stated by van Bemmelen (*Zeitsch. anorg. Chem.*, 1894, 5, 466) to give undoubtedly crystalline products. Two separate samples of each were prepared. The Becquerel preparation was seen to consist in the one case, when microscopically examined, of pale blue, fine crystalline needles. For the second sample, a higher power instrument was used, and the preparation was seen to be composed of well formed prisms, with marked birefringence and certainly not pseudomorphs. No trace of colloidal matter could be detected. The crystals were slowly blackened by *N*-potassium hydroxide at 25°. *N*/2-Potassium hydroxide was practically without action, as also the *N*/10-alkali generally employed. At room temperature, *N*/1-alkali was without effect. When shaken

for some weeks at 25° with *N*/7-ammonium hydroxide they blackened. They were unaltered by being left over the week-end in a vacuum desiccator, and not affected by heating to 100° for ten minutes in an air-bath or in boiling water. On analysis, after being heated to 100°, they gave Cu = 63.94 (determined as copper), H₂O = 19.67 (loss on ignition), NO₃ = 0.04 per cent. (colorimetrically as NH₃).

$$\text{Ratio, } \frac{[\text{H}_2\text{O}]}{[\text{Cu}]} = 1.08.$$

The Böttger preparation was composed in both cases of particles of rather doubtful crystalline nature, and of very irregular shape and size. Some of them "stained" with methyl-violet solution, and many, when examined microscopically in polarised light, did not react. On heating, or on treatment with alkali, they behaved like the Becquerel preparation.

Analysis of material dried at 100° gave: Cu = 64.16; H₂O = 19.58; SO₄ absent.

$$\text{Ratio, } \frac{[\text{H}_2\text{O}]}{[\text{Cu}]} = 1.07.$$

Cu(HO)₂ requires Cu = 65.15; H₂O = 18.46 per cent.

The above figures agree closely with analyses quoted by van Bemmelen, who gives 19.4 per cent. of water in the Becquerel and 19.6 per cent. in the Böttger preparations. As he further states, the preparations are slightly hygroscopic. The fact that these substances contain some 8 per cent. more water than corresponds with the ratio 1CuO : 1H₂O, is of interest. van Bemmelen is inclined to attribute the discrepancy to the presence of amorphous material. This explanation might very well suffice for the case of the Böttger preparations, but certainly does not hold in the case of the definitely crystalline Becquerel products. The crystals are perhaps an admixture of cupric hydroxide and some higher hydrate. In that case one of the co-existing forms should disappear with time. Some of the preparation was accordingly shaken at 25° for some weeks in a dilute (*N*/7) solution of ammonia. The ammonia, by increasing the solubility, should increase the rate of disappearance of the unstable phase. The whole mass, however, dehydrated (see above), and no more material was at that time available. This observation rather points to the crystalline cupric hydroxide being unstable with respect to cupric oxide and water at room temperature, and the influence of electrolytes, such as ammonium hydroxide, potassium hydroxide, etc., in increasing the rate of loss of water might be possibly due to their solvent action depending on complex ion formation or the slightly amphoteric character of cupric hydroxide. Further investigation is being devoted to this question.

The cuprous oxide was prepared by reducing an alkaline copper sulphate solution with sucrose. The product, if rapidly and thoroughly washed, is very pure.

Metallic copper was prepared by reducing finely-powdered cupric oxide in a stream of hydrogen at a low temperature.

Hydrogen (for the hydrogen electrode) was prepared from pure zinc and dilute sulphuric acid; it was washed with silver nitrate solution and by concentrated alkaline potassium permanganate solution, passed through a tube packed with cotton wool, and finally bubbled through a wash-bottle containing the solution to be experimented on before entering the electrode vessel.

It was found that constant values for the electrodes were not obtained at once, but required in many cases considerable time. Further, it is necessary to protect both systems from access of oxygen, which materially alters their potentials. Electrode vessels of a simple type were used. They consisted merely of a tube about 20 cm. in length and 2 cm. in internal diameter, closed at the bottom and provided at the other end with a well-fitting rubber stopper. A side-tube, one-third way up, bent down at right angles and fitted with a tap, makes connexion with the other half element, whilst the electrode is sealed into a glass tube which enters through the rubber stopper. The electrodes used were of blank platinum (occasionally platinised) or freshly coppered platinum, the total area being 2 to 5 sq. cm. Connexions were made by means of mercury.

The auxiliary electrodes used were hydrogen electrodes (alkaline solution) and calomel electrodes of the ordinary type. Liquid potentials when existing were always calculated by means of the ordinary Planck formula. In the connecting vessel was used alkali of the concentration experimented on at the time, and this was frequently renewed.

The *E.M.F.*'s were measured by the Poggendorf method, and the apparatus used—metre bridge, Weston cadmium cell, and galvanometer—needs no particular description. All readings were taken at 17°, the prevailing room temperature.

In setting up an electrode the depolariser used (a mixture of either cupric hydroxide and cuprous oxide, or of cuprous oxide and copper) was filled into the electrode vessel to a depth of 1 or 2 cm., the electrolyte poured in, the tap (greased) closed when the side-tube had been filled, and then the electrode tube and rubber stopper inserted. These were finally pushed down with the tap open, and the latter closed only when all else was in position. One or two c.c. of air remained in the vessel. After thoroughly coating the rubber stopper with wax, the whole vessel was shaken overnight on an efficient shaker and connected up for measurement in the ordinary way. When

about to take a reading, the tap was opened—otherwise kept closed. On the first time of opening, a little alkali from the connecting vessel entered to replace the oxygen in the electrode vessel absorbed during shaking. This only happened once. Afterwards, all oxygen having disappeared, there was no further contraction. This simple apparatus acted very well, and the measurements were never disturbed by entrance of oxygen from outside. As already stated, the single potential differences did not become constant at once. They were read several times daily, the vessels shaken overnight, and values not taken as final until constant over three days.

It will be noticed that in the cells described above, there are no liquid potential differences. This advantage was, however, negatived when it was found that hydrogen electrodes in the alkali solutions do not behave well, but give inconstant values which indicate insufficient saturation of platinum by hydrogen, caused by slowness of absorption or by the presence of some depolarising agent. Nothing very certain appears to be known on this point. In the literature one finds conflicting statements. Thus, Smale (*Zeitsch. physikal. Chem.*, 1894, 14, 577) obtained at 17° in *N*/10-potassium hydroxide the value -0.749 volt; in *N*/10-sodium hydroxide the value -0.738 ; the theoretical value, assuming 90 per cent. dissociation, is -0.758 . With *N*-potassium hydroxide he found -0.785 ; with *N*-sodium hydroxide -0.789 ; whilst the theoretical value with sodium hydroxide, if the degree of dissociation is taken as 0.72, is -0.810 volt, and for potassium hydroxide -0.812 volt, assuming 76 per cent. dissociation. He attributed the discrepancies to impurities in the electrolytes. Wilsmore (*Zeitsch. physikal. Chem.*, 1900, 35, 291), who demonstrated the reliable behaviour of hydrogen electrodes in acid solutions, states that they are also constant in alkaline solutions. Johnson (*Trans. Amer. Electrochem. Soc.*, 1902, 1, 187) states that the hydrogen electrode in alkaline solution is exceedingly sluggish in reaching its final value. Lorenz and Hauser (*Zeitsch. anorg. Chem.*, 1906, 51, 81), on the other hand, seem to have had a rather different experience. Their values would appear to indicate supersaturation with hydrogen. Lorenz and Mohn (*Zeitsch. physikal. Chem.*, 1907, 60, 422), working with hydrogen electrodes in sodium and potassium hydroxide, of different concentrations, after eliminating by calculation the liquid potentials, obtained for the $\begin{array}{c} \text{Pt} \\ | \\ \text{H}_2 \end{array}$ alkali single potential difference values which showed considerable discrepancies. With potassium hydroxide were always obtained more negative figures than with sodium hydroxide. Thus with *N*-alkali, 0.006 volt; with *N*/10-alkali, 0.007 volt; with *N*/100-alkali, 0.029 volt; with *N*/1000-alkali, 0.011 volt; whereas in *N*-alkali the difference should be only

two milli-volts, and for the higher dilutions should not exist. The latest workers using the electrode are Luther and Pokorňý (*Zeitsch. anorg. Chem.*, 1908, 57, 290) and Brönsted (*Zeitsch. physikal. Chem.*, 1909, 65, 84). They give no single potential difference measurements but their experience was evidently a satisfactory one.

The author's results point to the electrode being an untrustworthy one. Working with *N*/10-alkali, he has generally obtained -0.748 to -0.754 volt (theoretical -0.758). Sometimes values far less negative were obtained, such as -0.735 . Sometimes values a few milli-volts more negative than the theoretical value were obtained, as -0.762 , although figures were never reached as much on the negative side of the theoretical as Lorenz and Hauser obtained with the *N*-alkali electrode. The readings were often attained slowly, and varied irregularly with time and the speed of the gas through the electrode vessel. Sometimes abnormal readings were obtained, such as -0.710 volt. These could be avoided by boiling the electrode in water immediately before use. And, generally speaking, this treatment tended to rapid setting up, more negative values, and more constant results. But the effect was by no means a certain one. Possible action of oxidising impurities in the alkali was eliminated. The influence of the presence of an oxide of platinum in the platinum-black of the electrode was at one time suspected, but this could not be proved, nor could the hypothesis be quite reconciled with the behaviour of the electrode on heating, boiling, etc. A few experiments were carried out using *N*-alkali. The results deviated considerably from the theoretical value, but it was noticed that during each separate experiment they showed better constancy.

Calomel electrodes were consequently used for the measurements described in this paper.

Results.

The experiments first described were carried out with *N*/10-alkali as electrolyte. Both sodium hydroxide and potassium hydroxide were used, and the half-elements were, as a rule, set up in duplicate. In stating the results, the conventions as to sign and zero already mentioned are used. The potential of the decinormal calomel electrode is taken as $+0.335$ volt at 17° , the liquid potential differences, *N*/10-potassium hydroxide and *N*/10 sodium hydroxide minus *N*/10-potassium chloride, as 0.015 volt and 0.020 volt respectively.

The following tables contain the results obtained :

TABLE I.—*Temperature = 17°.*

	←— Current in cell.	
	Hg Hg ₂ Cl ₂ N/10-KCl N/10-alkali Cu ₂ O Cu.	Cu Cu ₂ ON/10-alkali.
Alkali, NaOH	{ 0.598 volt }	- 0.283 volt
	{ 0.601 ,, }	- 0.286 ,,
Alkali, KOH	{ 0.605 ,, }	- 0.285 ,,
	{ 0.605 ,, }	- 0.285 ,,
	Mean.....	- 0.285 volt.

In the above table, the one column contains the *E.M.F.* of the actual working combination ; the other contains the single potential difference which constitutes the cathodic portion of the cell A (see p. 2152).

TABLE II.—*Temperature = 17°.*

	←— Current in cell.	
	Hg Hg ₂ Cl ₂ N/10-KCl N/10-alkali	
Cu(HO) ₂ (Böttger) :	Cu(HO) ₂ Pt.	Pt Cu(HO) ₂ N/10-alkali.
	Cu ₂ O	Cu ₂ O
In NaOH	{ 0.327 volt }	- 0.012 volt
	{ 0.328 ,, }	- 0.013 ,,
In KOH	{ 0.338 ,, }	- 0.018 ,,
	{ 0.333 ,, }	- 0.013 ,,
	Mean..	- 0.014 volt
Cu(HO) ₂ (Bequerel) :		
In NaOH	{ 0.329 volt }	- 0.014 volt
	{ 0.334 ,, }	- 0.019 ,,
In KOH	{ 0.343 ,, }	- 0.023 ,,
	{ 0.335 ,, }	- 0.015 ,,
	Mean.....	- 0.018 volt

In table II, the first column, as before contains the observed *E.M.F.*'s against calomel electrodes, whilst the second column contains the single potential difference which forms the cathodic component of the combination B (see p. 2152).

With the aid of the above values, and assuming that the reversible P.D. $\frac{Pt}{H_2} | N/10\text{-alkali}$ is - 0.758 volt at 17°, we calculate the following figures for the *E.M.F.*'s of the cells mentioned at the beginning of this paper.

Cell A.	Cu	Cu ₂ ON/10-alkali	Pt	0.473 volt
Cell B.			H ₂	
(Böttger Cu(HO) ₂)	Pt	Cu(HO) ₂ N/10-alkali	Pt	0.744 ,,
Cell B.			H ₂	
(Bequerel Cu(HO) ₂)	Pt	Cu(HO) ₂ N/10-alkali	Pt	0.740 ,,
			H ₂	

The effect of altering the concentration of the alkali was next studied. Experiments were carried out with *N*-sodium hydroxide

and *N*-potassium hydroxide, and the following tables contain the results. The potential of the *N*-calomel electrode at 17° is taken as +0.282 volt, and the liquid potential differences, *N*-potassium hydroxide minus *N*-potassium chloride and *N*-sodium hydroxide minus *N*-potassium chloride, as 0.015 volt and 0.020 volt respectively.

TABLE III.—*Temperature = 17°.*

		←—Current in cell.	
		Hg Hg ₂ Cl ₂ <i>N</i> -KCl <i>N</i> -alkali Cu ₂ O Cu.	Cu Cu ₂ ON-alkali.
Alkali	}	0.604 volt	-0.342 volt
NaOH		0.606 „	-0.344 „
		0.605 „	-0.343 „
		0.607 „	-0.345 „
Alkali		Mean.....	-0.344 volt
KOH	0.613 „		-0.346 „

TABLE IV.—*Temperature = 17°.*

		←—Current in cell.	
		Hg Hg ₂ Cl ₂ <i>N</i> -KCl <i>N</i> -alkali	Pt Pt Cu(HO) ₂ <i>N</i> -alkali, Cu ₂ O
Alkali	}	0.337 volt (Böttger)	-0.075 volt
NaOH		0.335 „ (Böttger)	-0.073 „
		0.336 „ (Bequerel)	-0.074 „
		0.337 „ (Böttger)	-0.075 „
Alkali		Mean.....	-0.074 volt
KOH	0.343 „		-0.076 „

Platinised platinum electrodes

A few points arising out of tables III and IV should be noticed. Firstly, the single potential difference values obtained with potassium hydroxide as an electrolyte are in both cases more negative than those given with sodium hydroxide. This can be directly ascribed to the greater OH' ion concentration in the potassium hydroxide solution, with its correspondingly smaller metal ion concentration. The difference, 2 milli-volts, is equal to the calculated* one. Secondly, in table IV, no difference can be detected between the behaviour of the Becquerel and Böttger preparations. Thirdly, two of the measurements in table IV were carried out with platinised instead of blank platinum electrodes. The results were the same.

If we now take, as before, the P.D.'s $\frac{\text{Pt}}{\text{H}_2}$ | *N*-NaOH as -0.810 volt and $\frac{\text{Pt}}{\text{H}_2}$ | *N*-KOH as -0.812 volt, we deduce the *E.M.F.* of cell A to be (0.810—0.344) or (0.812—0.346) volt—that is, 0.466 volt. Similarly, that of cell B is (0.810—0.074) or (0.812—0.076) volt, equal to 0.736 volt.

In both cases these values are six or seven milli-volts or so lower

* See also calculated values for hydrogen electrodes on page 2157.

than those given by the $N/10$ -electrodes. As the P.D. of the H_2 -electrode half-element in both cases is calculated, the discrepancies must lie in the experimentally determined electrode values. This is the case. Assuming the value $Cu | Cu_2O, N/10\text{-alkali} = -0.285$ volt to be correct, one would expect for $Cu | Cu_2O, N\text{-alkali}$ the value $-0.285 - 0.052$ volt = -0.337 volt, whereas -0.344 was the figure experimentally determined. Now, the electrodes of both types experimented on, in both alkalis and in both strengths of alkali, invariably commenced by giving a higher positive value than the final value quoted in the tables. This corresponds, in electrodes of the type $Pt \left| \begin{array}{l} Cu(HO)_2 \\ Cu_2O \end{array} \right. \text{alkali}$, with an initial Cu^{++} ion concentration greater than the equilibrium value, and in electrodes of the type $Cu | Cu_2O$ alkali to a corresponding large Cu^+ ion concentration.* The change with N -alkali was far more rapid, and, as we see, lower final values were obtained than those calculated, assuming the $N/10$ values to be correct. A possible explanation of the fall of potential may be that the initial values correspond with particles of very fine grain and therefore of greater solubility, and that these are gradually removed and re-deposited in larger size. This view derives support from the fact that both cuprous oxide and cupric hydroxide are slightly amphoteric and can function as weak acids. Their solubility as anion in the alkali will thus increase with the concentration of the alkali, and hence the rate of change to the stable form should increase with the increase of alkali concentration, which is exactly what happens. With $N/10$ -alkali the last stages of the change may proceed so very slowly that the values observed during the experiments may never quite have reached equilibrium values. To test further this hypothesis, one sample each of Böttger and Becquerel hydroxides were re-examined microscopically. The Böttger hydroxide contained a large mass of material of average size $0.5-0.8\mu$. The Becquerel hydroxide contained many particles $1-2\mu$ in length. A sample of cuprous oxide (beautifully crystalline) showed a few crystals only $<2\mu$. The great majority were of the order of 5μ . We know from the work of Hulett (*Zeitsch. physikal. Chem.*, 1901, **37**, 385) that in those cases which have been examined, the solubility of a powder containing particles of size $<2\mu$ is dependent on variations in that size. The most striking case is that of mercuric oxide, the solubility of which can actually be increased threefold by suitable mechanical treatment. In the case of both samples of cupric hydroxide, we can fairly suppose these influences to come into

* This fall in P.D. is still more marked with electrodes containing cupric oxide instead of cupric hydroxide as depolariser, experiments with which are now being carried out.

play. Whether cuprous oxide is also effected is less certain. Now let us finally consider the effect a reasonable increase in solubility would produce on the potential difference measured, and take as an example the Pt $\left| \begin{array}{l} \text{Cu}(\text{HO})_2 \\ \text{Cu}_2\text{O} \end{array} \right.$ alkali electrode. The process occurring here is



We see that an increase in the Cu^+ concentration would actually diminish the P.D. But we know that such an increase, if any, must be small. We will here neglect it. Consequently the single potential difference will be increased by $58 \log C$ milli-volts, where C is the ratio of the Cu^{++} concentration to the normal equilibrium concentration. To take an extreme case, suppose $C = 3$, as with the mercuric oxide mentioned above. Then increase of P.D. = $58 \times 0.477 = 27$ milli-volts. Giving C various smaller values, we obtain the following table:

TABLE V.

C.	Increase of P.D.
3	0.027 volt
2.5	0.023 "
2	0.017 "
1.5	0.010 "
1.2	0.005 "
1.1	0.002 "

If we assume that the values finally obtained with the N -alkali electrodes are correct, the final values of the $N/10$ -alkali electrodes are about seven milli-volts too high. Their average fall before being taken as constant was perhaps another 5—7 milli-volts. The depolarisers, therefore, in their initial states gave values 14 milli-volts too high. This would correspond with a value of C of about 1.7, which is quite conceivable. Only a small fraction of the original depolariser is supposed to have been in this finely-divided state.

For purposes of calculation, although the lower values for the $E.M.F.$'s of the elements A and B are probably the more trustworthy, we will take the mean of the two sets of figures, and obtain, therefore,

$$E.M.F. \text{ of } A = 0.469 \text{ volt.}$$

$$E.M.F. \text{ of } B = 0.738 \text{ volt.}$$

If the above values be now substituted in equations (1) and (2), the solubility products mentioned at the beginning can be calculated. Taking k_w (the dissociation constant of water) as 0.56×10^{-14} at room temperature, we obtain:

$$k_o \text{ (for cuprous oxide) } 1.0 \times 10^{-14}.$$

$$k_i \text{ (for cupric hydroxide) } 1.0 \times 10^{-19}.$$

The solubilities $\left(\frac{\text{gram-mols.}}{\text{litre}}\right)$ in pure water at 17° work out at 0.5×10^{-7} for cuprous oxide and 3×10^{-7} for cupric hydroxide, assuming both to be in solution as completely dissociated bases only.

We are now in a position to see clearly the essential instability of the system $\text{Cu} \mid \text{Cu}(\text{HO})_2$ alkali. For if K (see p. 2151) be taken as 0.5×10^{-4} (Bodländer and Storbeck) and k_i as 1.0×10^{-19} , then

$$\sqrt{Kk_i} = \sqrt{0.5 \times 1.0 \times 10^{-23}} = 2.2 \times 10^{-12}.$$

This considerably exceeds the value for k_o given above. Cuprous oxide will consequently be precipitated at the expense of the cupric hydroxide and the electrode copper.

It has already been pointed out that the element A is in reality an $\text{H}_2\text{-O}_2$ cell working with a low but definite oxygen pressure. And from its $E.M.F.$ can be calculated the dissociation pressure at 17°C. of the reaction :



Taking 1.232 volts as the $E.M.F.$ of the $\text{H}_2\text{-O}_2$ cell with both gases at atmospheric pressure, we have

$$0.469 = 1.232 + \frac{0.058}{4} \log p_{\text{O}_2}.$$

$$\begin{aligned} \log p_{\text{O}_2} &= -\frac{0.763 \times 4}{0.058} \\ &= -53.4. \end{aligned}$$

$\therefore p_{\text{O}_2}$ at $17^\circ = 3 \times 10^{-53}$ atmospheres for $2\text{Cu}_2\text{O} \rightleftharpoons 4\text{Cu} + \text{O}_2$.

From this value, using equations developed in Haber's "Thermodynamics of Technical Gas-Reactions," the author has calculated the temperature at which the dissociation pressure of this reaction would become equal to 0.21 atmosphere, the temperature, that is, at which cuprous oxide would commence to lose oxygen when heated in air. The simplified * equation 26 (page 69. English edition) gives as this temperature 1929°abs. , that is, 1656° . If use is made of equation 15 (page 61), in which variations in the reaction heat with temperature are taken into account, a slightly higher temperature will be obtained.† Thus at 1900°abs. the system according to equation 26 will have a pressure of 150 mm.; according to equation 15, one of 45 mm. only.

With these figures we will now compare values calculated by using the formula derived by Nernst. For dissociations in which oxygen is involved it runs :

$$\log p_{\text{O}_2} = \frac{-Q}{4.57T} + 1.75 \log T + C,$$

where $C = 2.8$.

* Constant involved = -39.2 .

† Constant involved = -46.1 .

Putting in $Q = 81600$ and $T = 290$,
we get $\log p_{O_2} = -54.5 = 55.5$.

Hence $p_{O_2} = 3 \times 10^{-55}$ atmospheres at 17° for $2Cu_2O \rightleftharpoons 4Cu + O_2$.

The agreement (comparing the logarithms) is remarkably good. But at higher temperatures it is still more striking. Stahl (*Metallurgie*, 1907, 4, 682), using the same formula, has calculated, as the author has done above, the temperature at which the pressure of the system becomes equal to 0.21 atmosphere. He gets the value 1662° , whilst using Haber's simplified formula and the results of the electromotive measurements, the almost identical value of 1656° has been obtained. We are unfortunately not in possession of any experimentally determined values. Foote and Smith (*J. Amer. Chem. Soc.*, 1908, 30, 1344) have recently shown that the dissociation pressure does not exceed 1 mm. at 1020° .

It should be pointed out, however, that any dissociation pressures which may be observed in the future will probably be greater than those calculated by the Nernst or Haber formulæ. The reason is that the calculated values refer to the equilibrium between cuprous oxide, superheated solid copper, and oxygen, whereas the experimentally determined figures would hold for cuprous oxide, fused copper saturated with cuprous oxide, and oxygen. Both because of its being fused and because of the dissolved oxide, the vapour pressure of the copper entering into the equation :

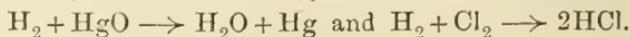
$$K = \frac{(p_{Cu})^4 \cdot p_{O_2}}{(p_{Cu_2O})^2}$$

will be less than in the calculated value, and hence the oxygen pressure correspondingly greater.

Apart from the dissociation pressure of the system $2Cu_2O \rightleftharpoons 4Cu + O_2$, there is another magnitude experimentally determined in this paper which can be calculated on the lines indicated by Nernst. That is the *E.M.F.* of the cell A, which corresponds with the reaction :

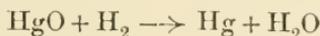


The first calculations of *E.M.F.*'s from thermochemical data, working with the Nernst thermodynamical theorem were made by Halla (*Zeitsch. Elektrochem.*, 1908, 14, 411). They only referred, however, to condensed systems of the type $Pb + 2AgCl \rightarrow PbCl_2 + 2Ag$. Nernst (*Sitzungsber. K. Akad. Wiss. Berlin*, 1909, 247) himself in a later paper has extended the calculations to electromotive systems in which gases can take part, such as correspond with the reactions :



To the first of these the element at present under discussion is strictly analogous. To avoid using in his calculation the specific heat of supercooled water, a quantity not accurately known, Nernst has

calculated the *E.M.F.* of the combination $\text{Hg} \left| \text{HgO alkali} \right| \frac{\text{Pt}}{\text{H}_2}$ at 0° , thus obtaining ice as one of the resultants of the reaction. He has compared the value obtained—0.880 volt—with a figure which is obtained by extrapolating Brönsted's (*loc. cit.*) results to 0° , namely, 0.934 volt. The discrepancy is thus rather considerable. In the present case, there are no available data from which the *E.M.F.* of the combination $\text{Cu} \left| \text{Cu}_2\text{O alkali} \right| \frac{\text{Pt}}{\text{H}_2}$ at 0° can be obtained. It was not thought worth while to measure the half-element $\text{Cu} \left| \text{Cu}_2\text{O alkali} \right|$ at 0° , because there are no existing figures on the temperature-coefficient of the hydrogen electrode or its value at 0° . This could, indeed, be calculated, but not with any great degree of certainty, from other existing data. That as a matter of fact it makes but little difference if the calculation does involve the specific heat of supercooled water can be readily shown. Thus for



we have

$$Q = 63200 - 21500 = 46700 \text{ at } 290^\circ \text{ abs.}$$

Also

$$\frac{dQ}{dT} = 3.5 + 2\beta.290 = 6.8 + 11.2 - 18.0 - 6.8 = -6.8.$$

$$580 \beta = -10.3. \quad \beta = -0.018.$$

Hence :

$$46700 = Q_0 + 3.5.290 - 0.018.(290)^2$$

$$Q_0 = 46700 - 1015 + 1514 = 47200.$$

Therefore :

$$E = \frac{0.0001983.290}{2} \left(\frac{47200}{4.571.290} - 1.75 \log. 290 + \frac{0.018.290}{4.571} - 1.6 \right)$$

$$= \frac{0.0001983.290}{2} (35.61 - 4.31 + 1.14 - 1.6^*)$$

$$= \frac{0.0001983.290}{2} (30.84) = \mathbf{0.887 \text{ volt.}}$$

This must be compared with the figure given by Brönsted for room temperature, namely, 0.929 volt.† We see that the discrepancy, although still considerable, is no worse, but rather less. The calculation of the *E.M.F.* of the cell $\text{Cu} \left| \text{Cu}_2\text{O alkali} \right| \frac{\text{Pt}}{\text{H}_2}$ is therefore carried out for room temperature.

The reaction is $\text{Cu}_2\text{O} + \text{H}_2 \rightarrow 2\text{Cu} + \text{H}_2\text{O}$.

* Nernst, *Zeitsch. Elektrochem.*, 1909, 15, 687.

† Measurements of the author (about to be published) give 0.925 volt for room temperature.

$$\begin{aligned} \text{We have} \quad & (\text{H}_2, \text{O}) = 68200 + (\text{H}_2\text{O}) \\ & (2\text{Cu}, \text{O}) = 40800 + (\text{Cu}_2\text{O}). \end{aligned}$$

$$\text{Hence} \quad Q_{290} = 27400.$$

The molecular specific heats involved are $(\text{H}_2) = 6.8$; $(\text{H}_2\text{O}) = 18$; $(\text{Cu}_2\text{O}) = 15.9$; $(2\text{Cu}) = 12.1$.

Therefore

$$\begin{aligned} \frac{dQ}{dT} &= 3.5 + 2\beta T = 6.8 + 15.9 - 18.0 - 12.1 = -7.4. \\ 2\beta T &= -10.9. \quad \beta = -0.019. \end{aligned}$$

Therefore

$$\begin{aligned} 27400 &= Q_0 + 3.5.290 - 0.019 (290)^2 \\ Q_0 &= 27400 - 1015 + 1600 = 27980. \end{aligned}$$

Hence

$$\begin{aligned} E &= \frac{0.0001983.290}{2} \left(\frac{27980}{4.571.290} - 1.75 \log. 290 + \frac{0.019.290}{4.571} - 1.6 \right) \\ &= \frac{0.0001983.290}{2} (21.11 - 4.31 + 1.20 - 1.6) \\ &= \frac{0.0001983.290}{2} (16.40) = \mathbf{0.472} \text{ volt.} \end{aligned}$$

The agreement is all that could be wished.

It should finally be mentioned that several workers have measured electrodes of the types described in this paper. For example, Immerwahr (*Zeitsch. anorg. Chem.*, 1900, **24**, 269), in her investigation of the copper ion concentrations in saturated solutions of sparingly soluble copper salts, used the combination $\text{Cu} \mid \text{Cu}(\text{HO})_2$ (colloidal) alkali. She found it impossible to calculate a solubility product for the cupric hydroxide, owing to the rapid change of potential. This was attributed to dehydration to cupric oxide, but it is obviously to be partly ascribed (in light of present results) to the change $\text{Cu}'' + \text{Cu} \rightarrow 2\text{Cu}'$. Lorenz and Hauser (*loc. cit.*) and Johnson (*loc. cit.*) have both worked with the electrode $\text{Cu} \mid \text{Cu}_2\text{O}$ alkali. For the combination $\text{Cu} \mid \text{Cu}_2\text{O}$ alkali $\left| \begin{array}{c} \text{Pt} \\ \text{H}_2 \end{array} \right.$, the former workers found values of 0.905 to 0.932 volt, whilst Johnson found 0.438 volt; both figures are considerably different from the 0.469 volt given in this paper.

Summary of Results.

(a) The system copper-cupric hydroxide-alkali is shown to be unstable.

(b) Cells containing the stable systems copper, cuprous oxide, alkali and platinum, cupric hydroxide, cuprous oxide, alkali have been measured.

(c) Existing data as to the untrustworthiness of the hydrogen electrode in alkaline solution are confirmed.

(d) The solubility products of cuprous oxide and cupric hydroxide are calculated.

(e) The influence of size of grain of depolariser on electrode potentials is emphasised.

(f) The dissociation pressure at room temperature of the reaction $2\text{Cu}_2\text{O} \rightleftharpoons 4\text{Cu} + \text{O}_2$ is calculated, and shown to be in fair agreement with the value obtained by calculating with Nernst's formula.

(g) The temperature is calculated at which cuprous oxide will dissociate in air according to the above equation, and is shown to give the best of agreement with the same value obtained using Nernst's formula.

(h) The *E.M.F.* of the element $\text{Cu} \left| \text{Cu}_2\text{O alkali} \right| \begin{matrix} \text{Pt} \\ \text{H}_2 \end{matrix}$ has been calculated in the way shown by Nernst, and the result is again in excellent agreement with that experimentally determined.

The author wishes to offer his best thanks to Prof. Donnan for the continued interest shown, and the valuable advice given, during the course of this work.

MUSPRATT LABORATORY OF PHYSICAL CHEMISTRY,
UNIVERSITY OF LIVERPOOL.

CCXXXII.—*A New Synthesis of Oxazole Derivatives.*

By ROBERT ROBINSON.

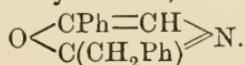
DURING the course of a synthetical investigation, the author had occasion to prepare ω -phenylacetyl aminoacetophenone,



and noticed that this substance, under the influence of concentrated sulphuric acid, readily loses the elements of water with the production of a feeble base of the formula $\text{C}_{16}\text{H}_{13}\text{ON}$. The probable explanation of this interesting change is that this compound, reacting in its enolic form,



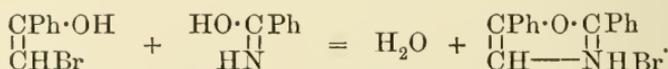
loses water from the two hydroxy-groups, and the base obtained would then be 5-phenyl-2-benzyloxazole,



That the reaction really does take this course was proved by examining ω -benzoylaminoacetophenone, a substance which was easily obtained by benzoylating ω -aminoacetophenone. On treatment with concentrated sulphuric acid, this compound was found to yield 2:5-diphenyloxazole, identical with the base prepared by Emil Fischer (*Ber.*, 1896, 29, 205) by the condensation of benzaldehyde with its cyanohydrin under the influence of hydrochloric acid. The same base is also obtained by heating bromophenylacetaldehyde with benzamide (E. Fischer, *Ber.*, 1896, 29, 213).

The production of 2:5-diphenyloxazole from ω -benzoylaminoacetophenone is a clear proof that in the synthesis of oxazoles from bromo-ketones or aldehydes and acid amides, the hydrogen of the amino-group condenses with oxygen of the carbonyl group rather than with the bromine. Thus, for instance, the reaction between bromoacetophenone and benzamide does not involve the intermediate formation of benzoylaminoacetophenone, since it is the 3:5- and not the 2:5-diphenyloxazole which is produced (Blümlein, *Ber.*, 1884, 17, 2580; Lewy, *Ber.*, 1887, 20, 2579).

The synthesis may be represented as follows if both the bromoacetophenone and the benzamide are assumed to react in the enolic form:

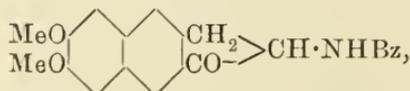


2:5-Diphenyloxazole and, to a much greater extent, its dimethoxy-derivative (see p. 2172), exhibit blue fluorescence in alcoholic solution.

The introduction of the methylene group between the oxazole ring and the phenyl radicle gives rise to oxazoles which are not fluorescent. Evidently the occurrence of this property is dependent on an uninterrupted chain of conjugate double linkings connecting the aromatic nuclei through the oxazole ring.

The method of synthesising oxazole derivatives described above in the case of 2:5-diphenyloxazole has been tested in various cases, and is probably of very general application, but at least one case in which ring formation does not take place has been observed.

2-Benzoylamino-5:6-dimethoxyhydrindone,



is unchanged by solution in sulphuric acid for half an hour, and this is remarkable in view of the ease with which the closely allied ω -benzoylaminoacetoveratrone undergoes the transformation. It is the author's intention to apply this method of oxazole formation to the

synthesis, not only of the unknown parent of the group itself, but also of some of its more important derivatives.

In the meantime a number of new substances are described, which it was necessary to prepare in order to test the applicability of the above synthesis.

EXPERIMENTAL.

ω-Benzoylaminoacetophenone, $\text{COPh}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{COPh}$.

This compound is very readily obtained under the following conditions: *ω*-Aminoacetophenone hydrochloride (5 grams) is dissolved in water (50 c.c.), the solution vigorously stirred, and treated with benzoyl chloride (7 grams) and sufficient aqueous potassium hydroxide (40 per cent. solution) to keep the liquid alkaline.

When all the benzoyl chloride has been decomposed, the oil solidifies. The almost colourless, crystalline mass is collected, washed with water, and a small quantity of oily impurity removed by contact with porous porcelain.

The colourless substance may be recrystallised from alcohol, and separates in beautiful needles, melting at 123° :

0.1202 gave 0.3322 CO_2 and 0.0608 H_2O . C = 75.4; H = 5.6.

$\text{C}_{15}\text{H}_{13}\text{O}_2\text{N}$ requires C = 75.3; H = 5.4 per cent.



Benzoyl-*ω*-aminoacetophenone (1 gram) was dissolved in concentrated sulphuric acid (5 c.c.), and the solution warmed on the water-bath for two minutes and then poured into water.

The colourless, crystalline precipitate, after collection and crystallisation from light petroleum (b. p. $50\text{--}70^\circ$), melted at 73° , whilst the melting point of 2:5-diphenyloxazole, prepared from benzaldehyde and benzaldehydecyanohydrin, is 74° (E. Fischer, *Ber.*, 1896, 29, 207). The identity of the two substances was further proved by a careful comparison of the products, as well as by the fact that a mixture of them melted at 73° .

Since 2-phenyl-5-veratryloxazole exhibits marked blue fluorescence in benzene solution, it was of interest to examine 2:5-diphenyloxazole in this respect.

It was found that, although this property is difficult to observe in ordinary light, yet by the light of burning magnesium the alcoholic or benzene solution of this substance shows strong violet-blue fluorescence.

ω-Phenylacetylaminacetophenone, $\text{COPh}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\text{Ph}$.

This substance was prepared in considerable quantities for some synthetical experiments, and the following process was found to be expeditious.

ω-Aminoacetophenone stannichloride (50 grams) is dissolved in hot water (250 c.c.) and the solution cooled, and treated with phenylacetyl chloride (30 grams) and then with aqueous potassium hydroxide (175 c.c. of a 40 per cent. solution). The rise in temperature is checked by the addition of small pieces of ice, and the liquid must be thoroughly stirred by mechanical means. The end of the reaction is indicated by the crystallisation of the product, and, after dilution with water, the pale yellow crystals are collected and crystallised from benzene, ether, or alcohol.

The purest product is obtained from ether; colourless needles or prisms, melting at 104° :

0.1235 gave 0.3424 CO_2 and 0.0680 H_2O . $\text{C} = 75.6$; $\text{H} = 6.1$.

$\text{C}_{16}\text{H}_{15}\text{O}_2\text{N}$ requires $\text{C} = 75.9$; $\text{H} = 5.9$ per cent.

The *oxime* crystallises from benzene or dilute alcohol in prisms, or from ethyl acetate and light petroleum as a highly characteristic mass of balls of minute threads. It melts at 154° , and was found to be unaltered by solution in concentrated sulphuric acid for a short time. Longer action induces some change, but it was not found possible to isolate the expected six-membered, heterocyclic substance.

On analysis, after drying in a vacuum:

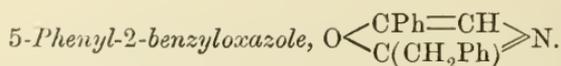
0.1217 gave 10.9 c.c. N_2 at 12° and 765 mm. $\text{N} = 10.7$.

$\text{C}_{16}\text{H}_{16}\text{O}_2\text{N}_2$ requires $\text{N} = 10.4$ per cent.

The *phenylhydrazone*, when recrystallised from alcohol, forms a beautiful, satiny powder, which under the microscope is seen to consist of curious crystals, shaped like a flower with four large petals. This derivative melts at 184 — 185° , and shows a great tendency to change into a yellow oil, especially under the influence of heat:

0.1222 gave 12.8 c.c. N_2 at 150° and 754 mm. $\text{N} = 12.2$.

$\text{C}_{22}\text{H}_{21}\text{ON}_3$ requires $\text{N} = 12.2$ per cent.



ω-Phenylacetylaminacetophenone (2 grams) was dissolved in cold concentrated sulphuric acid (10 c.c.), and the solution kept for two hours. On adding water in excess, a crystalline precipitate is obtained, but time must be allowed for the milky fluid to deposit the

whole of the substance in a solid condition. On crystallisation from light petroleum, magnificent long, flat needles, melting at 89° , separate.

In common with the other oxazole derivatives described in this paper, this substance is readily soluble in most organic solvents, but sparingly so in boiling water or cold light petroleum:

0.1300 gave 0.3891 CO_2 and 0.0639 H_2O . $\text{C} = 81.6$; $\text{H} = 5.5$.

$\text{C}_{16}\text{H}_{13}\text{ON}$ requires $\text{C} = 81.7$; $\text{H} = 5.5$ per cent.

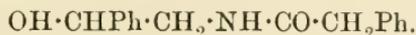
Under no conditions was fluorescence observed in the solutions of this substance.

The *picrate* forms pale yellow prisms, readily soluble in alcohol, melting at 103° :

0.1173 gave 11.6 c.c. N_2 at 10° and 768 mm. $\text{N} = 12.0$.

$\text{C}_{22}\text{H}_{16}\text{O}_8\text{N}_4$ requires $\text{N} = 12.1$ per cent.

α -Hydroxy- β -phenylacetyl-amino- α -phenylethane,



ω -Phenylacetyl-aminoacetophenone (10 grams) was dissolved in methyl alcohol (150 c.c.) and water (50 c.c.). The solution was vigorously stirred and treated with sodium amalgam (300 grams of 3 per cent.), added gradually during three hours. A neutral reaction was maintained by a stream of carbon dioxide, and the reduction was completed in four to five hours. The liquid was filtered to remove sodium carbonate, and then diluted with twice its volume of water. A crystalline precipitate slowly separated, which, when recrystallised, first from benzene and finally from dry ether, formed hard, colourless prisms, melting at 99° :

0.1198 gave 0.3291 CO_2 and 0.0747 H_2O . $\text{C} = 74.9$; $\text{H} = 6.9$.

$\text{C}_{16}\text{H}_{17}\text{O}_2\text{N}$ requires $\text{C} = 75.3$; $\text{H} = 6.6$ per cent.

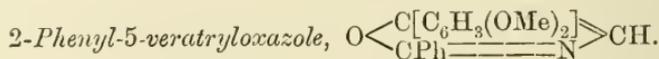
Unsuccessful attempts were made to cause this substance to give up the elements of water so as to produce a dihydro-oxazole derivative. Thus the action of concentrated sulphuric acid is either so mild that the compound may be recovered unchanged, or so vigorous at higher temperatures that there is complete decomposition. If a solution in concentrated sulphuric acid is warmed for two minutes on the water-bath, then diluted with water and boiled, a very strong and characteristic odour of phenylacetaldehyde is observed. The formation of this substance is clearly due to the elimination of water so as to form the compound



which, in turn, is further hydrolysed, yielding phenylacetaldehyde, ammonia, and phenylacetic acid.

This alcohol is also surprisingly stable towards phosphoric oxide in boiling benzene solution. In one experiment a 10 per cent. solution in benzene was boiled for one and a-half hours with a large excess of phosphoric oxide. On decomposing the product with ice, a considerable quantity of the unchanged substance was found in the aqueous phosphoric acid solution, from which it was recovered by extraction with ether after the addition of sufficient alkali to neutralise the acid. Under, however, more vigorous conditions, a very small quantity of a base can be isolated. α -Hydroxy- β -phenylacetyl-amino- α -phenylethane (5 grams) was dissolved in benzene (50 c.c.), and boiled with phosphoric oxide (30 grams) for five hours. The benzene was then decanted, and the residue heated for three hours on the water-bath. The product was dissolved in water, filtered, and, after rendering alkaline with potassium hydroxide, extracted with ether. The ethereal solution was washed with dilute hydrochloric acid, and this aqueous solution treated with picric acid.

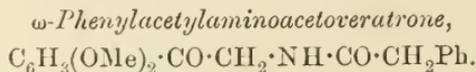
The *picrate* so formed crystallises from alcohol in canary-yellow micro-prisms, melting at 176—177°. There is a possibility that this substance is the *picrate* of benzylisoquinoline, which melts at 184° (corr.) (Decker and Pschorr, *Ber.*, 1904, 37, 3396). The quantity obtained was, however, very small, and the substance was not further investigated.



ω -Benzoylaminoacetylveratrone (1 gram) (Pictet and Gams, *Ber.*, 1909, 42, 2948) is warmed with concentrated sulphuric acid (5 c.c.) for five minutes on the water-bath. The solution is cooled, and decomposed by the addition of water. The oxazole derivative separates in colourless crystals, and on recrystallisation from light petroleum, forms groups of very slender needles, melting at 97°. The substance is readily soluble in alcohol or benzene, and the solutions show an intense blue fluorescence. It forms a rather sparingly soluble *hydrochloride*, which dissolves in warm water, and is apparently undissociated in presence of an excess of water. Thus the introduction of methoxy-groups has the effect of increasing the strength of oxazole bases :

0.1194 gave 0.3168 CO₂ and 0.0577 H₂O. C = 72.4 ; H = 5.4.

C₁₇H₁₅O₃N requires C = 72.6 ; H = 5.3 per cent.

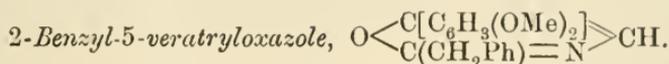


A solution of ω -aminoacetoveratrone stannichloride (25 grams) in hot water (150 c.c.) was cooled and treated with phenylacetyl chloride

(25 grams) and an excess of potassium hydroxide. The mixture was mechanically stirred, and cooled with small pieces of ice. The pale yellow, crystalline product was collected, and recrystallised from methyl alcohol, in which solvent it is sparingly soluble in the cold. Flocculent masses of needles are first obtained, and these change in course of time into a powder consisting of stout needles or prisms, melting at 135° :

0.1249 gave 0.3171 CO_2 and 0.0687 H_2O . $\text{C} = 69.2$; $\text{H} = 6.1$.

$\text{C}_{18}\text{H}_{19}\text{O}_4\text{N}$ requires $\text{C} = 69.0$; $\text{H} = 6.1$ per cent.

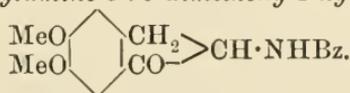


ω -Phenylacetylaminoveratrone (1 gram) was dissolved in cold concentrated sulphuric acid (5 c.c.). The solution becomes warm, and at the end of five minutes was diluted with water. The precipitated oxazole derivative, after collection and crystallisation from light petroleum, formed colourless needles, melting at 86° . It is fairly soluble in hot light petroleum, readily so in alcohol or benzene, but the solutions show no trace of fluorescence:

0.1272 gave 0.3410 CO_2 and 0.0703 H_2O . $\text{C} = 73.1$; $\text{H} = 6.1$.

$\text{C}_{18}\text{H}_{17}\text{O}_3\text{N}$ requires $\text{C} = 73.2$; $\text{H} = 5.8$ per cent.

2-Benzoylamino-5:6-dimethoxy-1-hydrindone,



2-Oximino-5:6-dimethoxy-1-hydrindone (10 grams) (Perkin and Robinson, *Trans.*, 1907, **91**, 1074) is treated with a solution of stannous chloride (40 grams) in concentrated hydrochloric acid (50 c.c.). In a short time the temperature rises, and the stannic chloride of the base separates out. After three hours, the precipitate is collected, dissolved in hot water, and the tin removed by means of hydrogen sulphide. The filtered solution, on evaporation, yields a crystalline mass of 2-amino-5:6-dimethoxy-1-hydrindone hydrochloride. On adding platonic chloride to a hot solution of the hydrochloride, the *platinichloride* is obtained in beautiful, golden needles:

0.1305 gave 0.0310 Pt. $\text{Pt} = 23.7$.

$(\text{C}_{11}\text{H}_{13}\text{O}_3\text{N})_2, \text{H}_2\text{PtCl}_6$ requires $\text{Pt} = 23.8$ per cent.

2-Amino-5:6-dimethoxy-1-hydrindone hydrochloride (3 grams) was dissolved in water (50 c.c.) and shaken with benzoyl chloride (10 grams), the solution being rendered alkaline by the addition of small quantities of aqueous potassium hydroxide. A colourless, chalky solid separated,

and was collected and washed with alcohol. To effect this it is necessary to grind the substance with the solvent in a mortar.

The product, when dried on porous porcelain, cements together to a very hard and brittle cake. It is sparingly soluble in most organic solvents, and crystallises from benzene, ethyl acetate, or alcohol in needles melting at 224°:

0.1251 gave 0.3175 CO₂ and 0.0646 H₂O. C = 69.2; H = 6.1.

C₁₈H₁₇O₄N requires C = 69.4; H = 5.5 per cent.

This *benzoyl* derivative was found to be unchanged by concentrated sulphuric acid or alcoholic hydrochloric acid, unless the temperature employed is so great that the substance undergoes profound decomposition.

THE UNIVERSITY,
MANCHESTER.

CCXXXIII.—*The Correction of the Specific Gravity of Liquids for the Buoyancy of Air.*

By JOHN WADE, D.Sc., and RICHARD WILLIAM MERRIMAN, B.A.

IN the course of an extensive series of specific gravity determinations, considerable difficulty was experienced in obtaining concordant results. The error was eventually traced to the correction for buoyancy of air, for which the customary formula (I) was employed. In this formula, w , W are the apparent weights of liquid and water respectively, $S_{t'/t}$ the corrected specific gravity of the liquid at t'/t , and ρ its true density at t' (= specific gravity at $t'/4^\circ$).

Correction Formula I.

$$S_{t'/t} = \frac{w}{W} \left(1 + \frac{0.0012}{\rho} - 0.0012 \right).$$

Investigation of the relative importance of the various sources of error led to the formulation of some very simple expressions, which will be found materially to reduce the labour involved in these troublesome corrections. It is assumed throughout that the pycnometer is filled with liquid and water at identical temperatures, either by means of a thermostat, or by reading the water-content of the pycnometer, for any temperature at which it may be filled with liquid, from a curve plotted from water-values at various other temperatures. The correction for the expansion of glass, which would otherwise be necessary, is not only troublesome to determine with

accuracy, but also renders it difficult to reduce the buoyancy correction to a reasonably simple form.

The expression (I) assumes a mean value for the density of air (0.0012), and is only valid when the pyknometer (or plummet), water, and liquid are weighed on a day on which the density happens to have this value. This condition is rarely complied with, and in a long series of determinations, during which the atmospheric conditions are constantly changing, errors may be introduced which fall within the limits of experiment.

The density (σ) of air half saturated with moisture is given in the following table, in which the temperature of the balance room is assumed to be between 10° and 25°, and the barometric pressure between 740 and 780 mm. (corr.). For dry air the values are a trifle greater, for saturated air a trifle less; the extreme difference in either direction is less than 0.00001.

TABLE I.

Weight of 1 c.c. of Air, σ , at ordinary Temperatures and Pressures.

Temperature.	Pressure in millimetres.				
	740.	750.	760.	770.	780.
25°	0.001146	0.001162	0.001177	0.001193	0.001208
20	0.001168	0.001184	0.001199	0.001215	0.001230
15	0.001190	0.001206	0.001222	0.001238	0.001254
10	0.001211	0.001228	0.001244	0.001261	0.001278

It will be seen that, under ordinary conditions, the value of σ may vary by nearly 12 per cent.; the minimum occurs in hot weather with a low barometer, the maximum in cold weather with a high barometer. The correction obtained by substituting these values for that in formula (I) may vary from +0.00032 to +0.00036 for a light liquid, such as ether ($\rho = 0.72$), and from -0.00096 to -0.00105 for a heavy liquid, such as sulphuric acid ($\rho = 1.84$). Hence, if the fifth figure of the specific gravity is to have significance, it is necessary to introduce the true value of σ into the correction.

For this purpose, the following expression, in which the apparent specific gravity (D) at $t^\circ/t^\circ (= w/W)$ is substituted for the corrected density (ρ) at $t^\circ (= S_{e,t^\circ})$, will be found more convenient than the first formula; the error introduced by the substitution is negligible (p. 2176).

Correction Formula II.

$$S_{e,t^\circ} = D (1 + \sigma/D - \sigma) = D + \sigma (1 - D).$$

The above formulæ are based on the implicit assumption that the pyknometer, liquid, and water are weighed under identical atmospheric conditions (footnote, p. 2179), and with this limitation, formula (II) gives correct results for any value of σ . When, however, as must

necessarily happen in a long series of determinations, the liquid and water are weighed under different conditions, a more comprehensive formula is required, or a further, and more serious, error may be introduced.

The full expression for the corrected specific gravity ($S_{t/t'}$) of a liquid at t°/t° , whether determined by pyknometer or by areometer, is given by the following formula, in which w , W are the apparent weights of the liquid and water at t° , D is the apparent specific gravity of the liquid at t°/t° ($=w/W$), B the density of the weights, and σ , σ' the density of the air at the time of weighing the liquid and water respectively.*

Correction Formula III.

$$S_{t/t'} = \frac{w \{1 + \sigma (1/D - 1/B)\}}{W \{1 + \sigma' (1 - 1/B)\}} = D \frac{1 + \sigma (1/D - 1/B)}{1 + \sigma' (1 - 1/B)}.$$

This formula involves the following assumptions :

(1) That variations in the apparent weight of the empty pyknometer are eliminated, or allowed for (see p. 2178).

(2) That in calculating the *weight of air displaced* by the various masses, the following differences are negligible :

- (a) the difference between the apparent and true weights of the various masses ;
- (b) the difference between the apparent specific gravity of the liquid (D) at t°/t° and its true density (ρ) at $t^\circ/4^\circ$;
- (c) the temperature variations in the density of the water.

For (a) the error is at most 0.12 per cent. on the correction ; this is at most ± 0.05 per cent. on the specific gravity, making a maximum resultant error of ± 0.06 per 100,000. For (b) the error is at most ± 0.05 per cent. on the specific gravity correction of 0.05 per cent.,

* Let W_1 , W_2 , W_3 , be the apparent weights of the pyknometer (1) empty, (2) filled with water, at t° , (3) filled with liquid at t° , when the density of the atmosphere is respectively σ'' , σ' , and σ . Let Ω_1 , Ω_2 , Ω_3 be the corresponding true weights ; v , V the true volume of the pyknometer, empty and full ; ρ , δ , B the true densities of the liquid, water, and weight respectively ; and w , W , D as above.

$$\begin{aligned} \text{Then} \quad \Omega_3 &= W_3 + \sigma (V - W_3/B) ; \\ \Omega_2 &= W_2 + \sigma' (V - W_2/B) ; \\ \Omega_1 &= W + \sigma'' (v - W_1/B) ; \end{aligned}$$

$$\text{and} \quad S_{t/t'} = \frac{\{W_3 + \sigma (V - W_3/B)\} - \{W_1 + \sigma'' (v - W_1/B)\}}{\{W_2 + \sigma' (V - W_2/B)\} - \{W_1 + \sigma'' (v - W_1/B)\}}.$$

$$\text{Putting} \quad V = v + (\Omega_3 - \Omega_1)/\rho = v + (\Omega_2 - \Omega_1)/\delta,$$

and assuming that, for the purpose of the correction,

- (i) Ω_1 , Ω_2 , $\Omega_3 = W_1$, W_2 , W_3 ,
- (ii) $\sigma'' = \sigma$ and σ'

in the numerator and denominator respectively,

- (iii) $\rho = D$ and $\delta = 1$,

this expression reduces to formula (III).

making a maximum resultant error of ± 0.03 per 100,000. For (c) at 25° the error is 0.33 per cent. on the buoyancy correction for the water; this is +0.11 per cent. on the weight of the water, making the resultant error at most +0.35 per 100,000 on the specific gravity; at 20° this falls to +0.22, and at 15° to +0.11 per 100,000.

Now the accuracy of a specific gravity determination is practically limited by temperature, which for ordinary purposes cannot be regulated more closely than 0.01° . For most organic liquids, this corresponds very nearly with 0.00001 in specific gravity; hence errors of less than 1 in 100,000 may safely be neglected. As the extreme aggregate error of formula (III), assuming that all individual errors are at a maximum and in the same direction, is +0.4 per 100,000, it follows that this formula is rigidly accurate for specific gravities within ordinary range, under ordinary conditions of temperature regulation. The assumption that the density of water, for the purpose of the buoyancy correction, is unity, is the only one that seriously affects even the sixth decimal place.

Introducing extreme values of D and σ into formula (III), and taking the density of the brass weights as 8.4,* it will be seen that the variations in the corrected specific gravity are still further within the limits of experiment. In the case of ether, for example, for which $D = 0.736$ at $0^\circ/0^\circ$ with σ and $\sigma' = 0.0012$, the extreme deviation from the true correction, namely, when $\sigma = 0.00115$ and $\sigma' = 0.00125$, or vice versa, is ± 0.00008 ; this would correspond with a variation of 0.08° in temperature, or, in a 50 c.c. pycnometer, of 0.004 gram in weight.†

The above formula, although much simpler than the rigid expression from which it is derived, is still rather cumbersome, and makes correction decidedly laborious. In a series of determinations, the labour may be materially lessened by plotting the true water-content of the pycnometer against temperature once for all, as already indicated. The weight of water can then be read for any temperature at which the pycnometer may have been filled with the liquid; and the trouble-

* Strictly speaking, the density of the weights ought to be determined experimentally, and the small weights reduced to brass by the usual calibration in air. As, however, variations in this constant affect only a small coefficient in the numerator and denominator of the correction factor by the same very small amount, their influence on the correction is altogether negligible. In the extreme case of $B = 8.6$, $D = 1.84$, with σ and σ' alternately at opposite extremes, the error does not reach the sixth decimal place of specific gravities within the above range.

†	D .	σ .	σ' .	Corrected sp. gr.
	0.73600	0.00115	0.00125	0.73624
		0.00120	0.00120	0.73632
		0.00125	0.00115	0.73640
	1.84000	0.00115	0.00125	1.83887
		0.00120	0.00120	1.83899
		0.00125	0.00115	1.83911

some alternatives of bringing the liquid to a standard temperature, or of determining the coefficient of expansion of the pyknometer itself, are avoided. Putting $W' = W \{1 + \sigma'(1 - 1/B)\}$ for the corrected weight of water at t° , and $D' = w/W'$ for the apparent specific gravity, calculated on the corrected weight of the water, formula (III) becomes:

Correction Formula IV.

$$S_{c/c} = \frac{w \{1 + \sigma (1/D' - 1/B)\}}{W'} = D' + \sigma - \sigma D'/B.$$

The values of σ required for this formula are given in table I (p. 2175), and those of $\sigma D'/B$ in table II (p. 2179). The error introduced by substituting D' for D in the correction is negligible (compare D and ρ , p. 2176). In both formulæ, however, it is assumed, as already stated, that variations in the apparent weight of the empty pyknometer are eliminated either by counterpoising the vessel permanently with glass, or by weighing it immediately before filling with liquid and water respectively (see footnote, p. 2176). If this is not done, the error passes by difference into the weight of the liquid, and must be allowed for. The allowance is most conveniently made by subtracting a small correction (table III) from the true weight of the vessel. As the apparent weight of a 50 c.c. pyknometer weighing 20 grams may fluctuate by 0.0006 gram, neglect of this precaution may, in the case of a liquid of specific gravity 0.736, cause an error of 0.00002.*

* If a glass counterpoise be employed, it may conveniently consist of a solid slab, adjusted to the required weight by grinding. It is sometimes stated that the counterpoise should have approximately the same area as the tared vessel, in order that error from hygroscopic moisture may be eliminated. In the authors' experience this is unnecessary; the corrected weight of a pyknometer which has been carefully wiped with a fine cambric cloth, and allowed to attain equilibrium in a fairly dry atmosphere, such as that of a balance case, is for practical purposes constant.

But while it is permissible to employ a simple glass counterpoise for the pyknometer, the use of a sealed counterpart, such as is employed in determining the densities of gases, leads to a very grave error, which hitherto has apparently escaped attention. It is true that the sealed vessel eliminates error due to *variations* in the density of the air, and thus, at first sight, simplifies formula (III) to:

$$S_{c/c} = D(1 - \sigma/B)/(1 - \sigma'/B);$$

but in so doing, it introduces a constant error, which far outweighs any due to variations in the atmospheric conditions.

This error arises from the impracticability of exhausting the pyknometer at the time that the weight of the counterpoise is adjusted, as is done as a matter of course when a counterpoise is made to a gas density flask. It follows that in the automatic subtraction of the apparent weight of the empty pyknometer from that of the filled vessel, not only is the weight of the empty vessel subtracted, *but also that of the air it contained at the time that the counterpoise was adjusted.* Hence this weight, $(V - v)\sigma''$, must be added to the apparent weights of the liquid and water after these have been corrected for the buoyancy of the air on the brass weights.

TABLE II.

 Values of $\sigma D'/8.4$.

D'	σ			D'	σ		
	0.00115.	0.00120.	0.00125.		0.00115.	0.00120.	0.00125.
0.7	0.000096	0.000100	0.000104	1.3	0.000178	0.000188	0.000194
0.8	0.000110	0.000114	0.000119	1.4	0.000192	0.000200	0.000208
0.9	0.000123	0.000129	0.000134	1.5	0.000205	0.000214	0.000223
1.0	0.000137	0.000143	0.000149	1.6	0.000219	0.000229	0.000239
1.1	0.000150	0.000157	0.000164	1.7	0.000233	0.000243	0.000253
1.2	0.000164	0.000171	0.000178	1.8	0.000246	0.000257	0.000268

TABLE III.

Difference between True and Apparent Weights of Glass Pyknometer
($\rho = 2.5$).

$\sigma =$	0.00115	0.00120	0.00125
Difference in milligrams per gram	0.323	0.337	0.351

The results afforded by the simplified formula (IV) differ from the standard correction only by a small figure in the sixth decimal place; and the calculation, once the water-content of the pyknometer has been plotted, is merely a matter of adding and subtracting numbers read from a table. Further simplification is possible, however. The terms $\sigma(1/B)$ and $\sigma'(1/B)$ in formula (III), which embody the correction for the buoyancy of the air on the weights, become identical when $\sigma = \sigma'$, and in such cases, being very small compared with the whole, disappear.* The divergence from the true correction therefore depends on the difference between σ and σ' , and is, in fact, numerically equal to $D(\sigma - \sigma')/B = 0.12 D(\sigma - \sigma')$. For the extreme values of σ and σ' already considered, namely, 0.00115 and 0.00125, this amounts to +1.2 parts per 100,000, a quantity only just within the experimental

As $V - v = w/D = W$, formula (III) then becomes successively:

$$S_{e'e} = \frac{w(1 - \sigma/B) + (V - v)\sigma''}{W(1 - \sigma'/B) + (V - v)\sigma''} = D \frac{1 + \sigma''/D - \sigma/B}{1 + \sigma'' - \sigma'/B}$$

Introduction of a sealed counterpoise under these conditions therefore, not only fails to eliminate the correction for the buoyancy of the air on the contents of the pyknometer, but actually renders the full correction more complicated. Taking a mean value of 0.00120 for σ'' , the error introduced by assuming that the factor for the buoyancy of air on the liquid and water is eliminated ranges from -0.00033 for sp. gr. 0.736 to +0.00102 for sp. gr. 1.84, or over a slightly wider range if the correction for buoyancy on the weights be neglected (see, for example, Squibb's determination of the density of alcohol, *J. Amer. Chem. Soc.*, 1893, 15, 126).

* Formula (III) then reduces to $S_{e'e} = D(1 + \sigma/D)/(1 + \sigma)$, which, when multiplied by $(1 - \sigma)/(1 - \sigma)$, becomes $S_{e'e} = D + \sigma(1 - D)$, that is to say, formula (II); the terms in σ^2 are insignificant.

limits.* When, as is usually the case, the difference between σ and σ' is not more than 0.00005, the term $1/B$ may therefore safely be dropped from formula (III), giving :

Correction Formula V.

$$S_{c,r} = \frac{w \{1 + \sigma(1/D)\}}{W(1 + \sigma')} = D \frac{1 + \sigma/D}{1 + \sigma'}$$

If now the water-content of the pycnometer be corrected for the weight of the air displaced by the water when $\sigma' = 0.00120$ (neglecting that displaced by the weights), this last condition is realised for all ordinary values of σ . And if the values thus obtained be plotted against temperature once for all, the correction of the apparent specific gravity in a series of determinations is reduced to a simple addition. Putting $W'' = W(1 + \sigma')$ for the weight of water at t° , corrected in this manner,† and $D'' = w/W''$ for the corresponding apparent specific gravity, formula (V) becomes :

Correction Formula VI

$$S_{c,r} = \frac{w \{1 + \sigma(1/D)\}}{W''} = D''(1 + \sigma/D'') = D'' + \sigma,$$

or the correction to be added to the apparent specific gravity, when this is calculated on the weight of water corrected for air displaced by the water ($\sigma' = 0.00120$), is the weight of 1 c.c. of air at the time of weighing the liquid. Variation in the apparent weight of the pycnometer, if not eliminated, must be allowed for as above (p. 2178).

The relative accuracy of the above expressions will be gathered from the following examples, in which identical data for the specific gravity of alcohol are reduced by the various methods. The apparent weight

*	<i>D.</i>	σ .	σ' .	Correction.	Difference from (III).
	0.736	0.00115	0.00125	+ 0.000230	- 0.000008
		0.00120	0.00120	+ 0.000316	(correct)
		0.00125	0.00115	+ 0.000403	+ 0.000008
	1.84	0.00115	0.00125	- 0.001149	- 0.000021
		0.00120	0.00120	- 0.001008	(correct)
		0.00125	0.00115	- 0.000867	+ 0.000021

† For a series of determinations, the corrected water values would be plotted against temperature once for all, as under formula (IV). If the water-content of the pycnometer has been determined when σ' is other than 0.0012, as in the example given below, the whole curve may readily be corrected by means of a constant from table II (p. 2179), the quantity $0.0012 W/B$ being added to the true weight of water, namely, $W + W\sigma' - W\sigma'/B$, in order to reduce it to the required partially corrected value with $\sigma' = 0.00120$. As $D = 1$ for water, the value of $(\sigma - 0.0012)/B$ from table II is $0.000138 - 0.000143$. Hence the corrected weight is $W + 0.00116 W - (0.000138 - 0.000143) W = 51.7200 + 0.0600 + 0.000005 \times 52 = 51.7803$.

(*w*) of the alcohol at 14·98°, with $\sigma = 0\cdot00123$, was 41·0716 grams, the weight of the empty pyknometer having been duly corrected. The apparent water value (*W*), 51·7200 at 14·98°, was read from a curve which had been plotted uncorrected with $\sigma' = 0\cdot00116$.

	Alcohol.	Water.	Ratio.	Correction.	<i>S</i> at t°/t° .
I.	41·0716	51·7200	0·794114	$\times 1\cdot000311$	0·794361
II.	41·0716	51·7200	0·794114	$+ 0\cdot000253$	0·794367
III.	41·0716	51·7200	0·794414	$\times 1\cdot000380$	0·794416
IV.	41·0716	51·7729*	0·793306	$+ 0\cdot001114$	0·794417
V.	41·0716	51·7200	0·794114	$\times 1\cdot000389$	0·794423
VI.	41·0716	51·7803*	0·793190	$+ 0\cdot001230$	0·794420
Full †	41·1292*	51·7728*	0·794417	—	0·794417

* Corrected value. † Footnote (p. 2176).

CHEMICAL LABORATORY,
GUY'S HOSPITAL, LONDON, S.E.

CCXXXIV.—*The Colouring Matter of Cotton Flowers.* *Gossypium Herbaceum. Part II.*

By ARTHUR GEORGE PERKIN.

SOME years ago (Trans., 1899, **75**, 825) it was shown that the flowers of the Indian variety of the cotton plant contained as a glucoside a hitherto unknown colouring matter, which was called gossypetin, but a lack of material did not allow of a more than cursory study of this compound. More recently (this vol., p. 1855), it has been observed that gossypetin also exists as a glucoside in the flowers of the *Hibiscus sabdariffa*, and the results of this later investigation have indicated that the true formula of this dyestuff is $C_{15}H_{10}O_8$ rather than $C_{16}H_{12}O_8$, which was originally proposed for it. There was evidence that the rather higher analytical figures formerly obtained arose from a contamination of the gossypetin with a trace of a similar yellow colouring matter containing a higher percentage of carbon, and it is considered likely that this may consist of quercetin. The formula and general reactions of gossypetin suggest that it is possibly a hexahydroxyflavone isomeric with myricetin (Trans., 1902, **81**, 205), but the study of this substance is certain to be difficult, because, even could the flowers be procured in abundance, the amount of gossypetin which they yield is very small. With the desire of further investigating this compound, some quantity of Egyptian cotton flowers were obtained through the kindness of Mr. W. Lawrence Balls, of the Khedival Agricultural Society of Cairo, and although as a result the original intention of the work could not be carried out, some interesting new products

have been obtained. The flowers (corollas) were gathered from the ground, where they had fallen a day or two after the flower had opened out. They all came from one field of Afifi cotton, which is the main Egyptian variety and resembles all the other Egyptian kinds in its general habit of growth and in its flowers, differing only as regards the tint. The flower is golden-yellow, with a crimson spot at the base of the petal; this spot is not, however, so large as it is in many varieties of *Gossypium herbaceum*, using the word to signify the Asiatic type of cotton with small, round-lobed leaves. The Egyptian cottons appear, according to the recent researches of Messrs. Fletcher and Balls, to be derived from natural crosses of brown Peruvian cottons with the Sea Island variety.

EXPERIMENTAL.

The flowers were digested with ten times their weight of boiling alcohol for six hours, and the pale brown extract was evaporated to a small bulk. The residual liquid deposited, on cooling, an orange-brown precipitate, which was collected and washed two or three times with alcohol (the filtrate and washings (A) being reserved for examination). This product, which, when allowed to dry, consisted mainly of a semi-crystalline powder, was possessed of strong tinctorial property, and was of a glucosidal nature. It dissolved fairly readily in cold water, and this rather unusual property suggested that it was probably a salt of the dyestuff, which, on examination, proved to be the case. As the use of acid for the neutralisation of the compound was, in the circumstances, to be avoided, an aqueous solution of the substance, which had been freed from insoluble matter by filtration, and from wax by agitation with ether, was treated with lead acetate, causing the production of a dull red-coloured precipitate, which was collected, the filtrate being colourless or nearly so and free from dissolved glucoside. The precipitate, after being very thoroughly washed with boiling water, was mixed to a thin cream with water, and decomposed by means of hydrogen sulphide; the mixture was then heated to boiling, and the lead sulphide removed by filtration. The dull orange-coloured liquid, on being kept in a vacuum, slowly deposited a mixture of crystals and gelatinous matter, and the evaporation was continued until nothing further separated. This product was collected and crystallised two or three times from water, and then consisted of a yellow, micro-crystalline powder, melting at 196—197°. As further purification in this manner but little affected the melting point, it was at first considered to be pure, but subsequent experiment proved that this was far from

being the case, and that the substance was in reality a mixture. A recrystallisation from methyl alcohol and water caused the melting point to rise to 213—215°, by a second treatment in this manner it fused at 231—233°, and by two crystallisations from pyridine and water a further rise to 245—246° then occurred. Finally, it was ascertained that the true melting point of this more sparingly soluble constituent of the mixture was 247—249° (uncorr.).

When deposited from aqueous liquids, this substance contains water of crystallisation, which is evolved at 100°, but is regained in contact with moist air for some days. For the purpose of analysis, a determination of the gain in weight thus experienced by the dried substance gave the most satisfactory result:

Found, $H_2O = 10.64$; 10.53 .

An analysis both of the dried (*a*) and undried glucoside (*b*) was carried out:

Found, (*a*) $C = 54.22$; $H = 4.76$; (*b*) $C = 48.82$; $H = 5.07$.

$C_{21}H_{20}O_{12}$ requires $C = 54.31$; $H = 4.31$.

$C_{21}H_{20}O_{12} \cdot 3H_2O$ requires $C = 48.65$; $H = 5.02$; $H_2O = 10.42$ per cent.

It consists of small, glistening, bright yellow plates, almost insoluble in cold and fairly readily soluble in boiling water. Its alkaline solutions possess a deep yellow tint; with aqueous lead acetate it gives a bright red precipitate, and with ferric chloride an olive-green coloration. The high melting point of this glucoside is remarkable, for such has been unusual in connexion with the hitherto described members of this special group. A study of its hydrolysis with mineral acids revealed that it possessed considerable stability in this respect, for when a solution of 0.766 gram of the substance in 500 c.c. of water was digested at the boiling point for one and a-half hours with addition of 1 c.c. of sulphuric acid, on cooling, 0.733 gram of a yellow powder separated, which, on examination, was found to consist almost entirely of unaltered glucoside.

In a second experiment, 0.6905 gram of the dried substance, dissolved in 100 c.c. of hot water, was boiled for fifteen minutes with addition of 1 c.c. of sulphuric acid, but as hydrolysis did not even then appear to have occurred, a further 2 c.c. of the acid was added, and the solution boiled for two hours. During the latter operation a dull yellow precipitate gradually separated, and this was collected and dried at 160°:

Found, $C_{15}H_{10}O_7 = 63.94$.

$C_{21}H_{20}O_{10}$ requires $C_{15}H_{10}O_7 = 65.08$ per cent.

Finally, it was observed that the most efficient strength of acid for the hydrolysis of the glucoside was 4 c.c. of sulphuric acid in

100 c.c. of water, and although a slight discoloration of the product had occurred after a two hours' digestion, this was not very material. An analysis of the air-dried substance by this method gave as follows:

Found, $C_{15}H_{10}O_7 = 58.05$.

$C_{21}H_{20}O_{10} \cdot 3H_2O$ requires $C_{15}H_{10}O_7 = 58.30$ per cent.

The product consisted of yellow needles, contaminated with a trace of a brown impurity, and on account of this it was first converted into its acetyl derivative, which formed colourless needles, melting at $191-194^\circ$.

The hydrolysis of this compound was carried out by means of sulphuric acid in the presence of acetic acid, in the manner usually employed in these investigations (Trans., 1905, **87**, 107):

Found, $C = 58.32$; $H = 3.97$; $C_{15}H_{10}O_7 = 58.75$.

$C_{15}H_5O_5(C_2H_3O)_5$ requires $C = 58.59$; $H = 3.91$;

$C_{15}H_{10}O_7 = 58.96$ per cent.

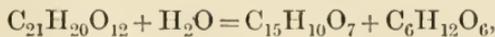
An analysis of the free colouring matter gave the following result:

Found, $C = 59.43$; $H = 3.64$.

$C_{15}H_{10}O_7$ requires $C = 59.60$; $H = 3.31$ per cent.

The examination of the properties of this substance indicated that it consisted of quercetin, and it was therefore evident that the compound $C_{21}H_{20}O_{12}$ is a hitherto unknown glucoside of this colouring matter. To identify, if possible, the sugar which is produced by the hydrolysis of this glucoside, the sulphuric acid present in the aqueous filtrate from the quercetin was removed by means of barium carbonate, and the clear liquid evaporated to dryness. The viscid residue was extracted with alcohol, the alcoholic solution evaporated, and the now almost colourless product was treated with phenylhydrazine in the usual manner. An osazone was thus obtained crystallising in needles, and this was collected and washed with a little ether. Considerable trouble was experienced in the complete purification of this substance by crystallising it either from alcohol or from alcohol and water, a point which has been referred to by Tutin (Proc., 1907, **23**, 250) as sometimes occurring with phenylglucosazone; but by the employment of alcoholic pyridine and water, as recommended by this author, the substance previously melting at $196-198^\circ$ then fused and decomposed at $204-205^\circ$. Owing to the small quantity of the glucoside which was available, it was not possible to examine the pure crystalline sugar, but, on the other hand, as a mixture of the osazone and phenylglucosazone also melted at $204-205^\circ$, there is every reason to consider that it consists of dextrose.

The hydrolysis of this glucoside, for which the name *quercimeritrin** is proposed, proceeds therefore according to the equation:



which requires a yield of 65.08 per cent. of quercetin.

When quercimeritrin is added to boiling acetic anhydride, it slowly dissolves, and if, after a two hours' digestion at this temperature, the solution is treated with its own volume of alcohol, colourless crystals of the acetyl derivative gradually separate out. The product is purified by recrystallisation from a mixture of alcohol and acetic acid:

Found, C = 55.31; H = 4.69.

$\text{C}_{21}\text{H}_{12}\text{O}_{10}(\text{C}_2\text{H}_3\text{O})_8$ requires C = 55.50; H = 4.50 per cent.

Acetylquercimeritrin consists of needles, which melt at 214—216°, and is very sparingly soluble in boiling alcohol.

A determination of the number of acetyl groups which this substance contains was carried out by the acetic ether method (Trans., 1905, **87**, 107), employing a solution of 3 c.c. of sulphuric acid in 30 c.c. of alcohol. At the conclusion of the operation, an examination showed that hydrolysis of the glucoside had also occurred, and the quercetin, which had been thus produced, was isolated by treating the residual alcoholic liquid with hot water and cautiously distilling off the greater portion of the alcohol:

Found, $\text{C}_2\text{H}_4\text{O}_2 = 61.07$; $\text{C}_{15}\text{H}_{10}\text{O}_7 = 37.76$.

$\text{C}_{21}\text{H}_{12}\text{O}_{10}(\text{C}_2\text{H}_3\text{O})_8$ requires $\text{C}_2\text{H}_4\text{O}_2 = 60.00$;

$\text{C}_{15}\text{H}_{10}\text{O}_7 = 37.75$ per cent.

It was therefore an octa-acetyl derivative.

Although quercimeritrin itself is almost insoluble in cold water, it has been shown above that it exists in these flowers, in a readily soluble condition, probably in the form of a salt. An examination of the residue given by an incineration of this plant product indicated the presence of a trace of iron, together with a considerable quantity of potassium, so that evidently the compound in question is mainly the potassium salt of the glucoside. A trace of copper was also present in the ash, but no importance could be attached to this point, because the alcoholic extraction of the flowers was performed in a copper vessel.

If a hot alcoholic solution of quercimeritrin is treated with potassium acetate, a yellow precipitate of a *potassium* salt at once separates. As this, when collected, congealed together, it was not completely freed from the excess of acetate by washing with alcohol:

* Derived from the "Quercimerinsäure" of Hlasiwetz and Pfaundler (*Jahresb.*, 1864, 569), the existence of which appears to be doubtful.

Found, $K=9.1$.

$C_{21}H_{19}O_{12}K$ requires $K=7.77$ per cent.,

but it was evidently a monopotassium compound, analogous to that which was previously prepared from rutin, a glucoside of quercetin (Trans., 1899, **75**, 439). This quercimeritrin compound was readily soluble in water, and almost insoluble in alcohol, and may be identical with the potassium salt of the glucoside which is present in the flowers.

The fact that quercimeritrin is an extremely stable glucoside is rendered obvious by a comparison of its behaviour in this respect with such well-known quercetin glucosides as quercitrin and rutin. These latter can be readily hydrolysed by digestion for about an hour with boiling dilute sulphuric acid of the concentration of 1 c.c. in 250 c.c. of water, whereas, as previously shown, quercimeritrin is best attacked by an acid which is ten times this strength.

On wool mordanted with aluminium, tin, chromium, and iron, quercimeritrin gave the following shades:

Aluminium.	Tin.	Chromium.	Iron.
Orange-yellow	Bright orange	Reddish-brown	Olive-brown

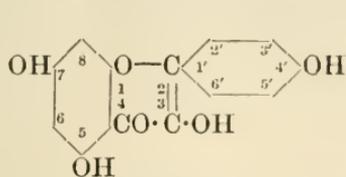
and these results were interesting, because, with the exception of the colour of the iron mordanted pattern, which is of a rather browner character, these shades closely resemble those which are given by quercetin* itself when dyed in a similar manner. On the other hand, they are widely different from the colours thus yielded by quercitrin and rutin, which have been described in an earlier communication (Trans., 1902, **81**, 480).

It has been previously pointed out (*loc. cit.*) that quercitrin is not hydrolysed during the dyeing operation, and it is most improbable that the more stable quercimeritrin would suffer decomposition during this process. The fact therefore that very similar shades are given both by the latter glucoside and quercetin itself is of importance, in regard to the location of the sugar nucleus.

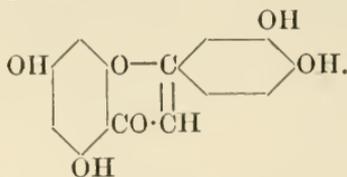
A study of the dyeing properties of kaempferol and luteolin (Trans., 1902, **81**, 590), employing woollen cloth, has shown that the colours given by the chromium, aluminium, and tin mordants are almost identical in each case. On the other hand, the dyeings produced by quercetin are not only stronger, but much redder than those characteristic of kaempferol and luteolin, and this result is evidently the joint effect of the 3'- and 4'-hydroxyl groups and the

* This was to be anticipated, owing to the fact that both this glucoside and quercetin yield, with lead acetate solution, similarly coloured precipitates.

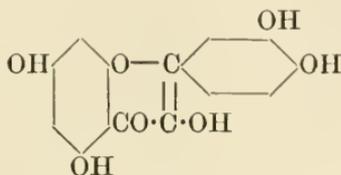
pyrone 3-hydroxyl group, contained by the former colouring matter. Again, it has been rendered certain by the location of the methoxy-



Kaempferol.

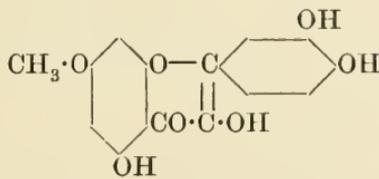


Luteolin.



Quercetin.

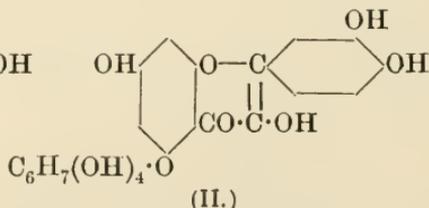
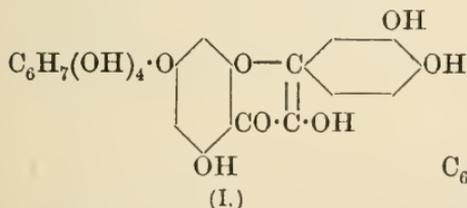
group in rhamnetin (quercetin monomethyl ether) (Trans., 1902, 81, 471):



Rhamnetin.

which dyes similarly to quercetin, that the hydroxyl groups present in the phloroglucinol nucleus have little or no effect as regards the shades produced from the latter compound.

There is every reason, therefore, to suppose that quercimeritrin contains the quercetin hydroxyl groups in the 3', 4', and 3-positions intact, and therefore its constitution will be represented by one of the two following formulæ:



The solution of this problem should not be difficult, and experiments on this point will be carried out as soon as the necessary quantity of the glucoside is available.

The alcoholic filtrate (A) (p. 2182), from which the crude potassium quercimeritrin had been removed, was treated with water, the alcohol evaporated, and the solution then agitated with ether

to remove waxy matter. The addition of lead acetate caused the formation of a deep red precipitate, which was collected, and the filtrate (B) placed aside for subsequent examination. When decomposed with hydrogen sulphide, this product gave, by the method above described, a further quantity of quercimeritrin, the identity of which was confirmed by analysis:

Found, C=54.00; H=4.48.

It has been previously shown that the purification of crude quercimeritrin is a matter of considerable difficulty, indicating that in this condition other compounds of a similar nature are present. To investigate this point, the combined mother liquors which had been derived from it were fractionally evaporated, and the deposits thus obtained were redissolved and submitted to a similar treatment. Eventually a middle fraction was isolated of a gelatinous nature, and this was allowed to dry, and digested with a little boiling acetic acid, which caused it to become granular, whereas the supernatant liquid acquired a rich dichromate colour. It was collected, again digested with the boiling acid, and, after extraction with methyl alcohol, repeatedly crystallised from dilute acetic acid. For analysis it was dried at 160°:

Found, C=52.50; H=4.31.

$C_{21}H_{20}O_{13}$ requires C=52.50; H=4.17 per cent.

It consisted of pale orange-yellow needles, melting at about 200—202°, very sparingly soluble in absolute alcohol or acetic acid. With aqueous lead acetate, it gives a deep red precipitate almost identical in appearance with that produced by quercimeritrin, and with ferric chloride an olive-green coloration. Alkalis dissolve it with a deep yellow tint, which becomes greener when the solution is diluted with water. As there could be no doubt that this substance was a glucoside, it was digested with boiling dilute sulphuric acid (1 c.c. in 25 c.c. of water) for two hours. During the reaction, crystals slowly separated, and after keeping overnight these were collected and weighed:

Found, $C_{15}H_{10}O_8$ =65.60.

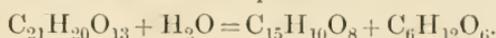
$C_{21}H_{20}O_{13}$ requires $C_{15}H_{10}O_8$ =66.25 per cent.

This product formed glistening, yellow needles, which dissolved with a green colour in very dilute alkali, and appeared to be gossypetin. To settle this point, an acetyl derivative was prepared; this consisted of colourless needles, melting at 226—228°, and was without doubt identical with acetyl-gossypetin.

The sugar produced by the hydrolysis of this glucoside was isolated in the usual manner, and an osazone prepared from it. This was obtained in yellow needles, which, after crystallisation

from alcoholic pyridine and water, melted at 203—205°, and was most probably phenylglucosazone.

The hydrolysis of *gossypitrin*, the name which is proposed for this glucoside, can therefore be represented as follows:



As but slightly less than one gram of this compound has as yet been isolated, it was not possible to investigate its acetyl derivative or its dyeing properties. Similarly, however, to quercimeritrin, it appears to be a somewhat stable glucoside, and it is likely that further experiment will show that the sugar nucleus occupies an analogous position in both these compounds. That *gossypitrin*, like quercimeritrin, also exists in these flowers as a potassium salt follows from its method of preparation.

The aqueous filtrates and other residues obtained during the isolation of this latter glucoside yielded, on further treatment, a gelatinous mixture, from which but a trace of sparingly soluble substance could be isolated by means of acetic acid. As a further separation appeared to be very difficult, especially as the quantity of the material available was small, it was dissolved in water and hydrolysed by the addition of sulphuric acid (1 c.c. in 25 c.c. of water), and digestion at the boiling point for two hours. A dull yellow-coloured precipitate gradually separated, which was collected, and converted into hydrochloride by means of hydrochloric acid in the presence of boiling acetic acid, and the semi-solid mass of red needles, which thus separated, was collected, washed with acetic acid, and decomposed with water. The product thus purified proved to be a mixture, the constituents of which were best separated in the form of their acetyl compounds. By repeated crystallisation, first from alcoholic acetic acid and subsequently from acetic anhydride, a small quantity of a very sparingly soluble acetyl derivative was isolated, which melted at 229—230°, and had the properties of acetyl*gossypetin*. This was hydrolysed by means of hydrochloric acid, and gave the following result:

Found, $C_{15}H_{10}O_8 = 55.50$.

$C_{15}H_4O_8(C_2H_3O)_6$ requires $C_{15}H_{10}O_8 = 55.78$ per cent.

The free colouring matter, as was anticipated, was found to be *gossypetin*:

Found, C = 56.71; H = 3.41.

$C_{15}H_{10}O_8$ requires C = 56.60; H = 3.14 per cent.

The more soluble constituent of the acetylated mixture, which proved to be the main bulk of this product, was obtained in colourless needles, melting at 191—194°, and consisted of acetyl*quercetin*.

That the original condition of the *gossypetin* thus prepared from

the plant was the glucoside gossypitrin above described seems probable, but, on the other hand, it cannot be considered that the quercetin isolated in such comparatively large amount had been produced by the hydrolysis of quercimeritrin. That so sparingly soluble a substance should have resisted isolation by the methods given above is not probable, and this point will be further investigated.

A study was now made of the aqueous filtrate from the second lead precipitate, and this, on treatment at the boiling point with basic lead acetate, gave a small quantity of a bright yellow precipitate. This was collected, suspended in water, and decomposed with hydrogen sulphide, and the mixture filtered hot. The pale yellowish-brown filtrate slowly deposited gelatinous nodules, and after several days these were collected and allowed to drain. This product, in the moist condition, was dissolved in a little boiling acetic acid, and the crystals, which separated on cooling, were recrystallised from dilute acetic acid, from water, and finally from pyridine and water:

Found, C=54.09; H=4.64.

$C_{21}H_{20}O_{12}$ requires C=54.31; H=4.31 per cent.

It consisted of pale yellow needles, melting at 217—219°, which were much less highly coloured than those of quercimeritrin, and in this respect somewhat resembled rutin. It is almost insoluble in cold and but sparingly in boiling water, soluble in alkaline solutions with a deep yellow tint, but its most interesting property is the fact that with aqueous lead acetate it gives a bright yellow precipitate entirely distinct from the deep red deposit which is produced in this manner from quercimeritrin. Again, this yellow lead compound is fairly readily dissolved in the moist condition by hot dilute acetic acid, whereas the quercimeritrin lake is much more stable under this treatment. With dilute alcoholic ferric chloride, it gives a deep olive-green coloration.

An important distinction between the two glucosides is observed also by an examination of their behaviour during hydrolysis, for when *isoquercitrin*, the name proposed for this new compound, is submitted to the action of boiling dilute sulphuric acid (1 c.c. in 25 c.c. of water), a crystalline product rapidly separates, and the reaction is quickly completed. On the other hand, the comparative stability of quercimeritrin in these circumstances has been previously discussed.

The following result was given by the hydrolysis of *isoquercitrin*:

Found, $C_{15}H_{10}O_7 = 64.56$.

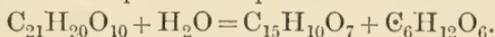
$C_{21}H_{20}O_{12}$ requires $C_{15}H_{10}O_7 = 65.08$ per cent.

The product consisted of yellow needles, soluble in dilute alkalis

with a yellow coloration, and on acetylation gave an acetyl compound, which formed colourless needles, and melted at 191—194°. Further experiment indicated that this colouring matter was quercetin.

The sugar produced during the hydrolysis of this glucoside was isolated in the usual manner, and converted into osazone. This, when purified by crystallisation from alcoholic pyridine and water, consisted of yellow needles, melting at 203—205°, which, when admixed with pure phenylglucosazone, did not affect the fusion point of the latter, and thus appeared to be identical with it.

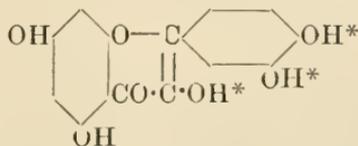
The hydrolysis of *isoquercitrin* proceeds therefore as follows:



Dyeing experiments with this glucoside, employing mordanted wool, gave interesting results, because the shades produced were entirely distinct from those given by quercimeritrin, but, on the other hand, somewhat closely resembled those yielded by quercitrin, although slightly paler (Trans., 1902, **81**, 480):

Chromium.	Aluminium.	Tin.	Iron.
Brownish-yellow	Golden-yellow	Lemon-yellow	Brownish-olive

It is quite evident, therefore, that although quercimeritrin and *isoquercitrin* are isomeric, and when hydrolysed give identical products, they are distinct substances. For reasons previously discussed, and alluded to elsewhere (Trans., 1902, **81**, 210), it is clear that the sugar group in the latter glucoside is not attached to the phloroglucinol nucleus, but is probably constituted like quercitrin, which on hydrolysis yields, however, rhamnose. Three formulæ are possible for *isoquercitrin*, which may be briefly expressed by the statement that the position of the sugar residue in respect to the quercetin group is at one or other of the points in the following formula which are marked with an asterisk:



Further experiments with regard to *isoquercitrin* have not been at present possible, for the total amount as yet obtained has been merely one gram, but it has been ascertained that its acetyl derivative is much more soluble in alcohol than the quercimeritrin compound. In the hope of isolating a larger amount of this substance, an extract of the flowers, to which a small quantity of acetic acid had been added, was treated with lead acetate, and the precipitate removed, but the quantity of *isoquercitrin* present in the filtrate did not appear to be thereby increased.

The mother liquors obtained during the purification of this glucoside yielded nothing but quercetin (Found, C=59.45; H=3.49), and this result was further corroborated by the preparation of its acetyl derivative (Found, C=58.21; H=4.22), which melted at 191—194°.

General Properties of the Flowers.

The results of this investigation have shown that Egyptian cotton flowers contain three hitherto unknown glucosides, quercimeritrin, *isoquercitrin*, and gossypitrin, of which the first-named has been isolated in by far the largest amount.

To ascertain approximately the total amount of yellow colouring matter which could be produced from this sample of flowers, 100 grams of the material were exhausted with boiling water, and the glucosides present in this solution hydrolysed by means of acid. The mixture was then repeatedly extracted with ether, the ethereal solution evaporated, and the residue collected and washed with water. There was thus obtained 1.86 grams, or 1.86 per cent. of the crude colouring matter, consisting of a mixture of quercetin and gossypetin, and this, when acetylated and the product fractionally crystallised from a mixture of alcohol and acetic acid, gave 0.3 gram of pure acetylgossypetin (Found, C=56.68; H=4.30), which corresponds with 0.165 gram of gossypetin itself. Such a process of separation is, however, far from exact, but it seemed evident that not more than 10 per cent. of the total colouring matter consisted of gossypetin. Dyeing experiments carried out with the flowers themselves in the usual way gave shades which, although duller, were somewhat similar in character to those yielded by quercimeritrin, a result indicating that no great quantity of *isoquercitrin* could be present:

Chromium.	Aluminium.	Tin.	Iron.
Reddish-brown	Green-yellow	Orange-brown	Olive-brown

In comparison with the colours similarly produced from other natural dyes, these shades most nearly resemble those of the so-called "Patent Bark," a preparation of quercitron bark, in which quercetin and no quercitrin is present. Further experiment indicated that in colouring power two parts of the bark were about equal in strength to five parts of the flowers, and this result was to be anticipated, for it was ascertained some time ago that the former dyestuff contains on the average 5 per cent. of quercetin.

The fact that quercetin is the predominating colouring matter of the Egyptian cotton flowers suggests that in this respect it may differ from the Indian variety, which was first examined, for in

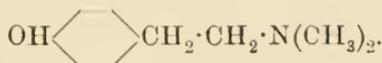
the latter case (*loc. cit.*) the presence of gossypetin only was detected. It has, however, been shown in this present work that the main constituent of the Egyptian material, quercimeritrin, is not readily susceptible to hydrolysis by acid, and it is possible that under the former experimental conditions the main bulk of this glucoside, if present, escaped decomposition. Through the kindness of Mr. I. H. Burkill, Reporter on Economic Products to the Government of India, a considerable quantity of the Indian material will be shortly available for investigation, and an opportunity will arise, not only for a study of the constitution of gossypetin, but for a direct comparison of the two varieties of flower, a matter which appears to be of considerable interest.

CLOTHWORKERS' RESEARCH LABORATORY,
THE UNIVERSITY,
LEEDS.

CCXXXV.—*Synthesis of Hordenine, the Alkaloid from Barley.*

By GEORGE BARGER.

A FEW years ago Léger (*Compt. rend.*, 1906, **142**, 108) isolated from barley germs a crystalline alkaloid, which he named hordenine, and subsequently (*Compt. rend.*, 1906, **143**, 234, 916) gave the following constitution:



This constitutional formula was confirmed by Gaebel (*Arch. Pharm.*, 1906, **244**, 435), and the physiological action of hordenine was studied by Camus (*Arch. int. de Pharmacodyn. et de Thé.*, 1906, **16**, 43).

It is evident that hordenine (*p*-hydroxyphenylethyldimethylamine: α -dimethylamino- β -*p*-hydroxyphenylethane) is closely related to *p*-hydroxyphenylethylamine, a physiologically active base of somewhat wide distribution, and the author's recent synthesis of the latter base (this vol., p. 1123) suggested an attempt to prepare hordenine from it by methylation.

This attempt was not wholly successful, for although the methiodide of hordenine was readily obtained by treating *p*-hydroxyphenylethylamine with methyl iodide, it was found impossible to isolate the alkaloid itself; the reaction did not stop at the tertiary base, but resulted in the formation of the quaternary iodide, no

matter what proportion of methyl iodide was employed. For the same reason it was found impossible to prepare α -dimethylamino- β -phenylethane, $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot NMe_2$, by direct methylation of the corresponding primary amine, for the only products formed were the primary and quaternary iodides. The same difficulty was recently encountered by Johnson and Guest (*Amer. Chem. J.*, 1909, **42**, 340).*

A suitable material for the synthesis of hordenine was, however, found in phenylethyl alcohol (benzylcarbinol), a commercial product, from which α -chloro- β -phenylethane could be prepared. The latter substance yielded, with dimethylamine, the desired α -dimethylamino- β -phenylethane. After nitration of this tertiary base, the *p*-nitro-compound was isolated as the oxalate. It was also found possible to obtain pure α -chloro- β -*p*-nitrophenylethane by distillation and crystallisation, and then to combine it with dimethylamine. On reduction the separation of the amino-compound from the unchanged nitro-compound proved difficult, since both substances are bases; the crude reaction-product was therefore diazotised, and finally yielded a small quantity of a base, identical with hordenine, prepared from malt germs.

EXPERIMENTAL.

α -Chloro- β -phenylethane, $C_6H_5 \cdot CH_2 \cdot CH_2Cl$.

Fischer and Schmitz have shown (*Ber.*, 1906, **39**, 2208) that, contrary to the statement of Fittig and Kiesow (*Annalen*, 1870, **156**, 245), the principal product of the chlorination of ethylbenzene is the α - and not the β -compound. They therefore used instead α -bromo- β -phenylethane, $C_6H_5 \cdot CH_2 \cdot CH_2Br$, which may be prepared according to Grignard's method (*Compt. rend.*, 1904, **138**, 1049). This method is, however, not very simple, and the required compound may be obtained more readily from phenylethyl alcohol (benzylcarbinol) (a commercial product, which is prepared synthetically, because it occurs in rose-oil).

By heating this alcohol with hydrogen chloride, only a small yield of the desired compound was obtainable; thionyl chloride and phosphorus pentachloride furnished a larger proportion, but the

* The phenylethylmethylamine prepared by these authors has been obtained in the course of the present work by reduction of the condensation product of phenylacetaldehyde with methylamine, $C_6H_5 \cdot CH_2 \cdot CH:NMe$. It is, of course, also readily obtainable from α -chloro- β -phenylethane and methylamine in the manner described below for the preparation of the dimethyl derivative; its *p*-nitro-derivative was prepared from α -chloro- β -*p*-nitrophenylethane and methylamine. A number of closely related bases containing one or two phenolic hydroxyl groups will soon be described.

product was contaminated with sulphur and phosphorus compounds. The best yield was obtained with phosphorus pentachloride as follows.

Dry chloroform (100 c.c.) was poured on phosphorus pentachloride (41.7 grams), and phenylethyl alcohol (24.4 grams = one molecular proportion) was added drop by drop. Much hydrogen chloride was evolved, and the phosphorus pentachloride gradually passed into solution; the reaction was completed by warming on the water-bath for two hours. After removal of the chloroform and phosphoryl chloride, the residue distilled under atmospheric pressure at 190—200° with slight decomposition. On redistillation under 20 mm. pressure, the bulk of the product boiled at 91—92°, and was approximately pure (yield = 70 per cent.):

0.2611 gave 0.2732 AgCl. Cl = 25.8.

C_8H_9Cl requires Cl = 25.2 per cent.

α-Dimethylamino-β-phenylethane, $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot N(CH_3)_2$.

Three grams of the above chloride were heated in a sealed tube with 4 c.c. (a considerable excess) of a 33 per cent. alcoholic solution of dimethylamine to 100° for several hours, and yielded 2.5 grams of the base, boiling at 198—202°. As so little was available, this substance was not further characterised, but the whole was nitrated.

α-Dimethylamino-β-p-nitrophenylethane,
 $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot N(CH_3)_2$.

2.5 Grams of the compound just described were added drop by drop to 10 c.c. of nitric acid (D 1.5), cooled to -10°. On diluting with ice, rendering alkaline, and extracting with ether, a syrupy mixture of nitro-derivatives was obtained. By adding an ethereal solution of anhydrous oxalic acid to the syrup, dissolved in ether, an *oxalate* was precipitated, which, after repeated crystallisation from 95 per cent. alcohol, formed elongated leaflets, melting at 153—154°. This salt is very sparingly soluble in hot absolute alcohol, but dissolves readily in dilute alcohol. The yield was 60 per cent.:

0.2130 gave 0.3989 CO_2 and 0.1094 H_2O . C = 51.0; H = 5.7.

$C_{10}H_{14}O_2N_2 \cdot C_2H_2O_4$ requires C = 50.7; H = 5.6 per cent.

That the nitro-group is in the para-position follows from the conversion of the substance into hordenine. The same salt was obtained from *α-chloro-β-p-nitrophenylethane* and dimethylamine, as follows.

*α -Chloro- β -*p*-nitrophenylethane, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2\text{Cl}$.*

α -Chloro- β -phenylethane (13 grams) was dropped into nitric acid (50 c.c.; D 1.5), cooled by a freezing mixture. After pouring on snow, extracting with ether, and washing the ethereal solution with sodium carbonate, the residue was distilled under 18 mm. pressure. Two fractions, b. p. 165—175° and 175—179°, were collected; the second of these crystallised almost completely on cooling below 0°, and was then drained on a porous tile in the cold room. After recrystallisation from light petroleum, 3.9 grams of glassy crystals were obtained, melting sharply at 49°:

0.1354 gave 9.2 c.c. N_2 (moist) at 17° and 758 mm. $\text{N} = 7.9$.

0.1593 „ 0.1195 AgCl. $\text{Cl} = 18.8$.

$\text{C}_8\text{H}_9\text{O}_2\text{NCl}$ requires $\text{N} = 7.6$; $\text{Cl} = 19.1$ per cent.

That the crystalline nitro-compound is the *p*-compound is a priori probable; that this is indeed the case follows from its conversion into α -dimethylamino- β -*p*-nitrophenylethane, which at once yielded an oxalate, melting at 153—154°, and identical with that described above.

*Conversion of α -Dimethylamino- β -*p*-nitrophenylethane into Hordenine.*

2.7 Grams of α -dimethylamino- β -*p*-nitrophenylethane oxalate were dissolved in 10 c.c. of alcohol; 2 grams of tinfoil and 10 c.c. of concentrated hydrochloric acid were added; after rendering alkaline with excess of sodium hydroxide, and extraction with ether, 0.55 gram of the crude amino-compound was obtained as a syrup. This was dissolved in 5 per cent. sulphuric acid, and to the boiling solution the calculated quantity of sodium nitrite was gradually added. Much resin was formed; on cooling, the filtered solution was rendered alkaline with sodium hydroxide, washed with ether, sodium carbonate added, and the solution extracted with ether. The ethereal extract left, on evaporation, a small quantity of crystals (m. p. 111°) and a little resin. On again dissolving the crystals in ether, the phenolic amine was extracted with sodium hydroxide, and afterwards shaken with ether; on evaporation of the ether, yellow crystals separated, which were drained on a porous tile and recrystallised from a mixture of benzene and light petroleum. In this way a small quantity of a white, crystalline substance was obtained, melting at 117—117.5°. A specimen of pure natural hordenine melted at 117.5°, and a mixture of equal quantities of the synthetic and the natural substance at 117—117.5°.

The synthetic specimen gave Millon's reaction very intensely; it reddened phenolphthalein, was not coloured by concentrated sulphuric acid, and reduced acid potassium permanganate in the cold and ammoniacal silver nitrate on warming; in all these respects its properties were identical with those of the natural base, as described by Léger. The amount of the synthetic substance obtained was insufficient for analysis.

The natural hordenine, used for comparison, was purified by distillation, the boiling point being 173—174°/11 mm. As in the case of *p*-hydroxyphenylethylamine, distillation is by far the most convenient method of purification.

Preparation of Hordenine Methiodide from p-Hydroxyphenylethylamine.

Two grams of *p*-hydroxyphenylethylamine were dissolved in a little methyl alcohol, and boiled for a few minutes with a large excess (20 c.c.) of methyl iodide. After two days, glassy prisms separated, which were up to 4 cm. in length; the weight was 0.45 gram, much being left in the mother liquor. On recrystallisation from water, the quaternary iodide gave stout crystals, melting at 230—231°, and closely resembling natural hordenine methiodide, a specimen of which melted at 229—230°; on mixing the two, the melting point was 229—230°:

0.1444 gave 0.1110 AgI. $I=41.5$.

$C_{11}H_{15}ONI$ requires $I=41.3$ per cent.

Benzoylhordenine methiodide,



was prepared from both specimens of hordenine methiodide; in each case hexagonal leaflets were obtained, sparingly soluble in hot water, and melting at 252—254°; this was also the melting point of the mixture of the synthetic and natural substance.

Although hordenine methiodide can thus be readily prepared from *p*-hydroxyphenylethylamine, numerous attempts to synthesise the alkaloid itself by this method were unsuccessful, and the other method, described above, had to be employed.

WELLCOME PHYSIOLOGICAL RESEARCH LABORATORIES,
HERNE HILL, LONDON, S. E.

CCXXXVI.—*Volumetric Estimation of Sulphates.*

By ALEC DUNCAN MITCHELL and CLARENCE SMITH.

A RAPID and accurate method for the volumetric estimation of sulphates is a much-needed process. All of these methods depend on the use of standard barium chloride solutions, but the exact determination of the end-point is a matter of difficulty. The method we are about to describe avoids this difficulty, and depends on the well-known ferricyanide end-point. After some preliminary work, our attention was called to a paper (*Zeitsch. anal. Chem.*, 1879, **18**, 521) in which Precht advocates an essentially similar method; but as we encountered difficulties which he appears not to have noticed, and as he gave no details of his process, we continued our investigation.

A convenient quantity of a sulphate is taken and dissolved in water or pure hydrochloric acid, or, if necessary, dilute nitric acid, and a slight excess of standard ($2N/5$) solution of barium chloride is added. The mixture is boiled and rendered neutral by ammonium hydroxide; sodium acetate, acetic acid, and a slight excess of $N/10$ -ammonium dichromate are added. The mixture is made up to 100 c.c., and the precipitate allowed to settle; 25 c.c. of the clear supernatant liquid are titrated with $N/20$ -ferrous ammonium sulphate, using potassium ferricyanide as an external indicator, and taking the first appearance of a green tinge as the end-point.

Preliminary experiments were made in which it was found that if ammonium dichromate is added to a solution of barium chloride, a certain amount of barium chromate remains in solution, owing to the formation of free mineral acid, but this does not happen if there is excess of sodium acetate, that is, if the solution is neutral or acidified by acetic acid.

Precht makes no mention of the fact that barium chromate dissolves in dilute solutions of strong acids, and does not state that he used neutral or alkaline solutions. Also he used a standard solution of potassium chromate, which is much more difficult to keep than one of the dichromate, being attacked by carbon dioxide. We found it advisable to use ammonium dichromate, as, apparently, barium chromate, on being precipitated by potassium dichromate, carries down with it traces of the potassium salt; the ammonium salt is much more soluble, and therefore preferable.

In the course of this work we used sulphuric acid (which was neutralised by ammonium hydroxide and hence was equivalent to ammonium sulphate), sodium sulphate, potassium sulphate, zinc

sulphate, magnesium sulphate, and copper ammonium sulphate. With potassium sulphate there is evidence of considerable adsorption (to the extent of nearly 2 per cent.), but this is minimised by boiling the precipitate for several hours with a little dilute hydrochloric acid (compare Sacher, *Chem. Zeit.*, 1909, **33**, 941), neutralising with ammonium hydroxide, and proceeding as before. Precht does not mention this difficulty, which is always met with in the gravimetric method also. In the case of sodium sulphate the adsorption is negligible, but is noticed slightly in the less soluble double sulphates, such as zinc ammonium sulphate and magnesium ammonium sulphate. The possibility of the formation of a double sulphate of barium and potassium has not been overlooked, and is rendered more probable from analogy to lead (Fox, this vol., p. 878).

This method is of wide application, since most chromates are soluble in acetic acid, and hence present no difficulty. Some, however, give a coloration with the potassium ferricyanide which obscures the end-point; copper is a case in point, but with a little practice it is possible to find a well-defined end-point at which a green tinge affects the predominating brown colour. Excluding weighings, five determinations can be made in an hour.

In the appended results, larger quantities are used than is usual, but the method applies for smaller quantities, as shown by the results obtained over a fair range, of which magnesium sulphate is given as an example; but in all cases the strength of the titrating liquids can be adjusted for convenience. The results recorded below are not selected; in each series the five experiments represent five consecutive determinations. It should be noted that ammonium dichromate, which is *N*/10 as regards oxidising power, is only *N*/30 as regards precipitating power.

A few determinations on potassium sulphate were made to find whether the adsorption was decreased by the use of standard baryta solution in place of barium chloride; this gave no better results.

Results.

I.—Estimation of Ammonium Sulphate (or Sulphuric Acid), in 2*N*/5-solution (26.43 grams per litre).

2 <i>N</i> /5-(NH ₄) ₂ SO ₄ taken, c.c.	2 <i>N</i> /5-BaCl ₂ , c.c.	<i>N</i> /10-(NH ₄) ₂ Cr ₂ O ₇ , c.c.	$\frac{1}{2}$ <i>N</i> /20-Fe(NH ₄) ₂ (SO ₄) ₂ , c.c.	2 <i>N</i> /5-(NH ₄) ₂ SO ₄ found, c.c.
20.10	20.54	4.05	0.88	20.16
19.99	20.26	3.50	0.95	19.99
20.15	20.68	4.77	0.81	20.15
*20.14	20.31	3.17	0.54	19.96
21.39	21.75	4.05	0.95	21.39

* This determination is obviously affected by some accidental error.

II.—*Estimation of Sodium Sulphate, in 2N/5-solution (28.43 grams per litre).*

2N/5-Na ₂ SO ₄ taken, c.c.	2N/5-BaCl ₂ , c.c.	N/10-(NH ₄) ₂ Cr ₂ O ₇ , c.c.	N/20-Fe(NH ₄) ₂ (SO ₄) ₂ , c.c.	2N/5-Na ₂ SO ₄ found, c.c.
20.04	20.32	3.88	0.64	19.89
20.05	20.17	2.12	0.29	19.91
20.19	20.59	3.98	0.88	20.22
20.12	20.70	6.10	1.09	20.05
20.10	20.56	3.89	0.91	20.22

III.—*Estimation of Zinc Sulphate, in 2N/5-solution (57.51 grams of ZnSO₄.7H₂O per litre).*

2N/5-ZnSO ₄ taken, c.c.	2N/5-BaCl ₂ , c.c.	N/10-(NH ₄) ₂ Cr ₂ O ₇ , c.c.	N/20-Fe(NH ₄) ₂ (SO ₄) ₂ , c.c.	2N/5-ZnSO ₄ found, c.c.
20.01	20.20	2.56	0.80	20.04
20.09	20.51	4.57	1.02	20.09
20.01	20.47	4.96	1.14	20.02
20.02	20.24	3.00	0.71	19.98
20.11	20.52	3.88	0.63	20.08

IV.—*Estimation of Magnesium Sulphate, in 2N/5-solution (49.30 grams of MgSO₄.7H₂O per litre).*

2N/5-MgSO ₄ taken, c.c.	2N/5-BaCl ₂ , c.c.	N/10-(NH ₄) ₂ Cr ₂ O ₇ , c.c.	N/20-Fe(NH ₄) ₂ (SO ₄) ₂ , c.c.	2N/5-MgSO ₄ found, c.c.
20.11	20.25	3.01	0.96	20.07
20.05	20.50	6.70	1.81	19.98
*19.95	20.69	4.40	0.58	20.15
20.01	20.40	4.89	1.26	20.00
20.05	20.31	5.89	1.97	19.98

* Bad determination.

The following determinations show that the method is equally applicable to smaller quantities.

2N/5-MgSO ₄ taken, c.c.	2N/5-BaCl ₂ , c.c.	N/10-(NH ₄) ₂ Cr ₂ O ₇ , c.c.	N/20-Fe(NH ₄) ₂ (SO ₄) ₂ , c.c.	2N/5-MgSO ₄ found, c.c.
5.03	5.67	5.91	1.15	5.07
9.70	10.12	3.88	0.81	9.74
15.11	15.35	2.31	0.53	15.14
19.88	20.08	2.00	0.24	19.83
25.00	25.61	4.56	0.37	24.97

V.—*Estimation of Copper Ammonium Sulphate, in 2N/5-solution (40.00 grams of CuSO₄.(NH₄)₂SO₄.6H₂O per litre).*

2N/5-CuSO ₄ .(NH ₄) ₂ SO ₄ taken, c.c.	2N/5-BaCl ₂ , c.c.	N/10-(NH ₄) ₂ Cr ₂ O ₇ , c.c.	N/20-Fe(NH ₄) ₂ (SO ₄) ₂ , c.c.	2N/5-CuSO ₄ .(NH ₄) ₂ SO ₄ found, c.c.
20.05	20.44	4.22	1.07	20.09
20.09	20.65	5.15	0.94	20.10
20.00	20.47	6.09	1.75	20.03
20.13	20.51	4.19	0.85	20.10
20.09	20.52	6.71	2.39	20.19

VI.—*Estimation of Potassium Sulphate, in 2N/5-solution (34.85 grams per litre).*

(Boiling for several hours with dilute hydrochloric acid is necessary.)

$2N/5\text{-K}_2\text{SO}_4$ taken, c.c.	$2N/5\text{-BaCl}_2$, c.c.	$N/10\text{-(NH}_4)_2\text{Cr}_2\text{O}_7$, c.c.	$N/20\text{-Fe(NH}_4)_2(\text{SO}_4)_2$, c.c.	$2N/5\text{-K}_2\text{SO}_4$ found, c.c.
20.12	20.48	5.59	1.50	20.05
20.08	20.27	3.95	1.55	20.13
20.03	20.53	5.26	1.06	20.01
20.52	20.60	5.36	1.61	20.24
20.17	20.67	6.33	1.33	20.06

That adsorption does take place without these precautions to the same extent as the discrepancy in the results is shown as follows. A hot solution of potassium sulphate is precipitated by just sufficient hot barium acetate solution, and the precipitate is filtered, dried, boiled with alcohol (to remove potassium acetate), filtered, and dried. A definite amount of the dry substance is boiled for several hours with dilute hydrochloric acid and a little sulphuric acid (which serves the double purpose of keeping the barium sulphate insoluble, and of producing the more soluble acid potassium sulphate from the normal sulphate); it is then filtered, washed with a little cold water, and dried. It is found that the potassium sulphate thus boiled out constitutes 1.37 per cent. of the total precipitate, or 1.83 per cent. of the original potassium sulphate.

EAST LONDON COLLEGE.

OBITUARY NOTICES.

BENNETT HOOPER BROUGH.

BORN 1860; DIED OCTOBER 3RD, 1908.

BENNETT HOOPER BROUGH was born at Clapham; his father, John Cargill Brough, a Fellow of this Society, was for some time editor of *The Chemist and Druggist*, subsequently he became librarian at the London Institute in Finsbury Circus, but after some years of ill-health he died in 1872. Brough and a younger brother and sister were left orphans; but their friends, including Michael Carteighe and William Chandler Roberts (afterwards Sir William Roberts-Austen), both Fellows of this Society, raised a fund for the education and maintenance of the children.

Brough was educated at the City of London School, whence he passed, in 1878, to the Royal School of Mines, and, having graduated as Associate in 1881, he went to the Royal Prussian Mining Academy of Clausthal, in the Harz district of Germany, to complete his technical training. In 1882, when he was twenty-three, Brough was appointed assistant to Sir Warrington Smyth, Professor of Mining at the Royal School of Mines, and four years later he instituted at the School a course in mine surveying, which he continued to direct with conspicuous success until his transference to the Iron and Steel Institute in 1893, when he took up the secretaryship of that Institute, a post which he retained until his death. His connexion with the Iron and Steel Institute had, however, started ten years before, and during the whole of that period his technical knowledge, literary skill, and linguistic capabilities had been exercised as an abstractor of the Journal of the Institute, and as an assistant and translator in the conducting of its foreign meetings. These talents were also applied to the Journal of the Chemical Society, for which Brough acted as abstractor from 1883 to 1895. Moreover, he served as a Member of the Council from 1895 to 1898. He was also a past Member of Council of the Institute of Chemistry and a Fellow of the Geological Society, and a Member of the Institution of Mining Engineers, of the Chartered Institute of Secretaries, and of the International Association for Testing Materials; in fact, of the three latter he

was again a Member of Council. He was likewise an active and welcome supporter of many foreign mining, metallurgical, and kindred technical associations.

His great powers of discrimination and discernment, added to his technical ability and general culture, combined, as they were in his case, with remarkable tactfulness, led to his services being sought in many directions; he, however, only accepted such work that would either assist him at his post or that would not, in any way, interfere with his work at the Institute, to which he was rigorously loyal and zealous. We find him serving on the Jury of several exhibitions, such as the Inventions Exhibition in 1885, the Paris Exhibitions of 1889 and 1900, the St. Louis Exhibition in 1904, and at the Franco-British Exhibition in London in 1908. He had acted as Examiner in Mining to the Board of Education, and as External Examiner to the Royal School of Mines, as well as to the Camborne School of Mines, whilst as a lecturer he was in great requisition throughout the United Kingdom, and occasionally abroad as well. At the International Congress of Applied Chemistry in Rome, he was selected as one of the Presidents. He delivered the Cantor Lectures at the Royal Society of Arts on several occasions; in 1892, on "Mine Surveying"; in 1900, on "The Nature and Yield of Metalliferous Deposits"; in 1903, on "The Mining of Non-metallic Minerals"; and in 1906 he delivered a course of juvenile lectures, at the Society, on "Perils and Adventures Underground." He was awarded the Society's Silver Medal for his paper on "Mining at Great Depths."

To technical literature, he was a prolific and valued contributor. In fact, in this direction his fine store of knowledge, his retentive memory, and a facile pen stood him in good stead. Among his numerous contributions may be cited "A Treatise on Mine Surveying," which appeared first in 1888, and has now reached the thirteenth edition. He contributed the articles on "Mining" to Chambers's *Encyclopædia*; the article on "Fuel" to Thorpe's *Dictionary of Applied Chemistry*; and many of his communications may be found in the Journal of the Iron and Steel Institute, in the Transactions of the Institution of Mining Engineers, as well as in other publications.

Brough had many social qualities, which endeared him to a large circle of friends. He was a staunch friend, ever ready to help those who sought his advice, and in case of the breakdown of a comrade he would, with characteristic readiness, energy, and whole-heartedness, either single-handed or in co-operation with others, at once put into action a scheme of relief, and would not rest until his object had been achieved. He had a subtle, mellow

vein of humour, tinged with a kindly cynicism; he was often tempted to use these attributes in his writings and lectures, but he generally reserved them for private life and after-dinner speeches, in which he excelled. He was a capital host, with exceptional gifts as a raconteur, an accomplishment he occasionally exercised in many languages, to the astonishment of those who had met him for the first time.

In 1895 he married Barbara, daughter of Edward Lloyd, barrister-at-law, whom he has left with two young children, a boy and a girl.

Brough was suddenly seized with acute gastric pains on October 1st, 1908, at Middlesbrough, during one of those successful meetings of the Iron and Steel Institute which became a feature of his tenure of the office of Secretary to that Institute. His illness necessitated immediate removal to a nursing home at Newcastle-upon-Tyne, where he succumbed to the exhaustion following an operation, on October 3rd, 1908.

Brough's death has caused a blank which is not easily filled. Many are they who miss his genial and stimulating comradeship, and still more who feel the loss of his ever-ready assistance and advice.

D. A. LOUIS.

RICHARD JOHN FRISWELL.

BORN FEBRUARY 24TH, 1849; DIED FEBRUARY 6TH, 1908.

RICHARD JOHN FRISWELL, who was born in London, was the eldest son of James Hain Friswell, a well-known essayist and novelist, perhaps best remembered now as the author of "The Gentle Life." His mother was an artist and a frequent exhibitor at the Royal Academy.

He was educated at private schools in London and near Southampton. As a possible outlet for the disposition he showed towards science, more especially chemistry, he was, on leaving school, at first placed as an articled pupil with a well-known photographer, Mr. Valentine Blanchard; but photography as a profession did not appeal to him, and he attended evening classes at King's College in chemistry and other subjects; finally he was allowed to follow his inclinations, and he went as a student to the Royal College of Chemistry. On completing his studies there, under Prof. Frankland and William Valentin, he became assistant to Dr. W. J. Russell, then Professor of Chemistry, at St. Mary's Hospital.

In 1871 Friswell took part in the Indian eclipse expedition, under Mr. (now Sir Joseph) Norman Lockyer. Successful as the expedition was, the day of the eclipse was for Friswell one of bitter disappointment. He was placed at Manantoddy, in charge of the analysing spectroscope. "Unfortunately," to quote Lockyer's words, "to the regret of all, Mr. Abbay and Mr. Friswell, who were among the best prepared for doing good work, and were at a station at which everybody said cloudless weather was certain, found themselves in a storm of cloud and mist which obscured the sun." Later he was again asked to take part in another eclipse expedition, that to the Andaman Islands in 1875, but he was not then able to leave London.

As a result of the co-operation in the 1871 expedition, Friswell, in August, 1872, became research assistant to Norman Lockyer, with whom he remained for the next two years. Under Lockyer's direction he assisted in numerous spectroscopic researches, in many of which his practical knowledge of photography was of much use. Amongst these may be instanced the first continuous series of observations on the solar chromosphere attempted in England.

In 1874 he was offered an appointment as research chemist in the Atlas Aniline Dye Works (Messrs. Brooke, Simpson and Spiller), at Hackney Wick, and for many years he took an active part in carrying on these works. In 1886, when the Atlas Works were converted into a limited company, he was made a director and chemical manager of the works; this post he held until 1899, when he became manager of the works of the British Uralite Company, at Higham, Kent, where he remained until 1902, when he started a practice in London as a consulting chemist and chemical engineer.

After his first paper on "A new double salt of Thallium" (this journal, 1871, **24**, 461, and also 1877, **32**, 251), Friswell's contributions to science were mainly concerned with the coal-tar colour industry; amongst these may be mentioned "On the relation of Diazobenzene to Amidoazobenzene" (Trans., 1885, **47**, 917, and also Proc., 1887, **3**, 26) and "The Constitution of Diazobenzene-anilide and its relation to Amidoazobenzene" (Trans., 1886, **49**, 746), both papers being published in collaboration with Prof. A. G. Green; "The Properties of Nitrobenzene" (Trans., 1897, **71**, 1010); "The Preparation of para-Toluidine from mixed Toluidines by means of para-Toluidine hydrate" (*J. Soc. Chem. Ind.*, 1908, **27**, 258).

Friswell served twice on the Council of the Chemical Society. He was an original member of the Society of Chemical Industry, and was chairman of its London Section from 1906 to the time of his death.

He was actively concerned in the inception of the Institute of Chemistry, and was elected a member of its first Council. Altogether he served fifteen years as member of Council of the Institute. He was also a Vice-President, 1896-1899, and Censor 1898-1899. He took an active part in the transfer of the Institute to its present quarters, and gave great assistance in the designing and organisation of its laboratories. For many years he acted as Chairman of the House Committee.

Friswell was Honorary Secretary of the Photographic Society 1874-1876, and Master of the Horners' Company 1894-1895.

Taken ill on the New Year's Eve with pleuro-pneumonia and enteric fever, he died after five weeks' suffering on February 6th, 1908.

Friswell married, in 1877, Millicent, daughter of W. H. Collingridge, and leaves a family of two sons and three daughters.

He was a man of wide tastes, both literary and artistic; his genial, enthusiastic, and kindly nature endeared him to all with whom he came into intimate contact, and on these he exercised a very wholesome influence.

A. J. G.

WILLIAM ASHWELL SHENSTONE.*

BORN DECEMBER 1ST, 1850; DIED FEBRUARY 3RD, 1908.

THE life of a schoolmaster is usually laborious, and when he devotes the greater part of his holidays to study and experimental research, little time is left for incident outside the daily routine. Shenstone's career was uneventful, but it brought him into frequent contact with the scientific world, in which he made many lasting friendships.

Born at Colchester on December 1st, 1850, he came of a family collateral with that of the poet, as it appears that his grandfather, Joseph Shenstone, born at Halesowen between 1790 and 1800, was a son of a cousin of that writer. W. A. Shenstone's father, James Burt Byron Shenstone, was established as a pharmacist at Colchester, and after the usual course of education at the Colchester Grammar School the son was received into the business. At the age of twenty he obtained, as the result of competitive examination, one of the Bell Scholarships, given annually by the Pharmaceutical Society. After a course of study in the School of that Society

* This notice is reprinted, by permission, from the *Proceedings of the Royal Society*.

he won the Pereira Medal and other prizes. During the time he was occupied in his father's business a portion of the premises was burnt down, and Shenstone was exposed to cold and damp, with the result that a serious illness followed, from the effects of which he never completely recovered. The injury which resulted was, in fact, the primary cause of his last illness nearly forty years later.

After two years spent in the laboratory of the Pharmaceutical Society, Shenstone accepted an engagement with Dr. W. A. Tilden, at that time chief science master at Clifton College. Here he displayed those qualities of patience, diligence, accuracy, and enthusiastic devotion to experimental work which distinguished him throughout life. In 1874 work was begun on the terpenes, at that time an unexplored department of organic chemistry, and Shenstone joined in the investigation with his usual ardour. The result was a paper, under the joint names of Tilden and Shenstone, published in the "Transactions of the Chemical Society," in which it was shown that the numerous hydrocarbons of this family then known were reducible to three classes according to the character of their nitroso-derivatives.

From Clifton, in 1875, Shenstone passed to the Science Mastership at Taunton School, then under the Head Mastership of the Rev. William Tuckwell. After about two years he moved to a similar position at Exeter School. Here he built and fitted up a school laboratory (described in *Nature*, July 26th, 1878) which attracted some attention, as it served to show that the practical teaching of physics and chemistry was within the reach of all properly conducted schools, and need not be avoided on the ground of expense, as had been up to that time so frequently alleged.

Shenstone was always an attractive lecturer, and interested himself much in educational problems, especially in connexion with the improvement of methods for teaching physical science. When, in 1880, he succeeded Dr. Tilden as Science Master at Clifton, he found a field in which he could bring into operation some of his ideas. Here he was one of the first science masters to associate practical work with all theoretical teaching, and here he made use of a modified "heuristic" system, in which an attempt is made to stimulate the disposition to inquiry which is inherent in most young minds. The extent to which this system in the hands of a competent teacher can achieve success is to some extent indicated by the very wide circulation of Shenstone's two books (*Practical Introduction to Chemistry*), and there can be no doubt that this pioneering work has materially influenced the teaching of natural science throughout the kingdom.

The greater part of his leisure was devoted to original research. During the earlier part of his time at Clifton he managed to carry out a difficult piece of work on ozone, and on the properties of certain highly purified substances, from which he drew important conclusions. The results of these experiments led him to the conclusion that chlorine, bromine, and iodine, when in the highest known condition of purity, and dried by contact under special conditions with phosphoric oxide for six months or more, do at once combine with mercury when brought into contact with that metal similarly purified and dried. The remarkable indifference displayed by some substances, when completely deprived of moisture, to the ordinary conditions of chemical change, had led some chemists to believe that it is impossible for any two substances to interact chemically except in the presence of a third substance, usually water, although only in minute quantity. The question must be regarded as still open, but it will be difficult for any future experimenter to improve on Shenstone's method or his manipulative skill.

Shenstone also joined Professor Tilden in a research on the "Solubility of Salts in Water at High Temperatures," the results of which form the subject of a paper in the *Philosophical Transactions* for 1884. In most of this work a good deal of complicated glass apparatus was required, and the whole of that which was needed in his work on ozone, on the purification of chlorine, etc., was constructed with his own hands. Shenstone was an accomplished glass blower, and in 1886 he published a small book, the first of its kind, giving instructions suitable for laboratory workers, which was translated into German, and is to be found in most chemical laboratories. Shenstone also succeeded in the far more difficult art of manipulating vitrified quartz, the properties of which he demonstrated in a lecture at the Royal Institution in 1901. Apparatus constructed of this material is of the utmost value in certain chemical and physical operations owing to the fact that it is unaffected by nearly all chemical agents except hydrofluoric acid, and that its coefficient of dilatation by heat is practically nil. Hence, unlike glass, it may be suddenly quenched in cold water from a red heat without injury. He devoted much time during the last two or three years of his life to the practical question of producing this material on a manufacturing scale, so as to bring it within the reach of scientific workers at a moderate cost, and to these efforts the physicists and chemists of to-day owe the beautiful clear variety of silica vessels now commonly in use.

Shenstone was elected into the Royal Society in 1898. In his later years he devoted some time to literary work, and produced

a *Life of Liebig* (Cassell and Co.), and the year before he died he gathered into one volume, under the title, *The New Physics and Chemistry*, a series of essays contributed to the *Cornhill Magazine*, in which he presented a remarkable and, on the whole, successful attempt to explain in popular language the modern views of physicists and chemists on subjects such as matter, motion, the ether, the nature of atoms and molecules, radioactivity, etc.

He married, in 1883, Mildred, daughter of the late Rev. Reginald Durrant, and he leaves a widow with a son and a daughter.

Shenstone possessed a fortunate combination of enthusiasm with peculiar skill in handling apparatus, and under more favourable conditions would certainly have done a much larger amount of scientific work. But what he did accomplish was a marvel to those who knew him well. In spite of the lameness, the cause of which has already been referred to, and which sometimes led to general disturbance of health, the brave, bright spirit, which endeared him to his friends, helped him over mountains of routine work, and kept him ever eager for the more attractive fields of science. He died at Mullion, Cornwall, on February 3rd, 1908, and is buried in the village churchyard.

W. A. T.

EDWARD SONSTADT.

BORN NOVEMBER 25TH, 1829; DIED JULY 5TH, 1908.

EDWARD SONSTADT, to whom metallurgy is indebted for the first successful production of the metal magnesium on a manufacturing scale, was born at Halesworth, in Suffolk, on November 25th, 1829. His father, Samuel Sonstadt, was a gentleman of private means, fond of reading and of studious tastes, but of feeble health and of nomadic habits, rarely living long in any one place. Owing to the failure of an American bank he lost the greater part of his fortune—about £40,000—and, emigrating to South Africa, died there in 1845. Young Sonstadt thus found himself at the age of sixteen in very straitened circumstances, and with a younger sister dependent upon him. To add to his anxieties, he was, at the time of his father's death, in poor health, enfeebled by long illness following upon an attack of brain fever. Indeed, all that he practically inherited from his father was a frail constitution and precarious health. Partly for this reason, and partly on account of the wandering life of the family, he received no regular or continuous schooling. Indeed, such was his physical condition

when a boy that it was never expected that he would reach manhood.

After his father's death Edward Sonstadt found his way back to England. Settling his scanty share of their joint inheritance upon his sister, the poor, frail, diffident youth now set himself to face the world with such courage as he possessed. And Sonstadt never lacked courage or self-reliance. He seems to have obtained employment for a time in a printing office, and to have tried his hand at book-keeping, and eventually at journalism. When eighteen years of age he migrated to Canada, where he procured a situation as proof-reader in the printing office of the Government Official Journal. Four years later he returned to England, recalled by his sister's illness. He remained in London for some years, picking up a precarious livelihood by his pen. At this period he was a frequent contributor to *Welldon's Scientific Register*. It was this connexion with scientific journalism which seems to have first induced him to turn his attention to chemistry, and he now devoted all his spare time to the study of that science. He then moved to Nottingham, where he acquired a small printing and book-selling business, and acted as librarian at some library in the town. Here he married Mary Lees, and shortly afterwards, when thirty-four years of age, removed to Manchester to work a patent he had secured for the manufacture of metallic magnesium. This metal, the existence of which was signalled by Davy, shortly after the discovery of the metals of the alkalis, was first definitely obtained by Bussy about 1829 by the action of potassium upon anhydrous magnesium chloride. Subsequently Bunsen prepared it by the electrolysis of the fused salt. Matthiessen, under Bunsen's direction, greatly improved the electrolytic method by substituting a mixture of the chlorides of magnesium and potassium for the anhydrous chloride, which is difficult to procure free from admixed oxide. He thus obtained considerable quantities of the metal, and was able to describe its leading properties.

At Deville's instigation Caron sought to place the manufacture of magnesium upon a commercial basis, but with no great success. Caron's process, which consisted in heating a mixture of magnesium chloride and fluorspar with metallic sodium, was costly to work, the yield was small, and the metal far from pure. Sonstadt greatly cheapened the process by the employment of carnallite—then available owing to the opening up of the Stassfurt deposits, and he devised a means of purifying the metal by distilling it. The fact that magnesium could be readily distilled was known to Deville and Caron, but Sonstadt was the first to employ this method of purification on a manufacturing scale. The process

was worked out in 1863 by Sonstadt in conjunction with the late Samuel Mellor, the founder of the Magnesium Metal Company, at Patricroft, near Manchester. It was at this period that the writer of this notice first made Sonstadt's acquaintance. He was a frequent visitor to the chemical laboratory of the Owens College, then in Quay Street, Manchester, the head of which, the present Sir Henry Roscoe, took great interest in the development of the new metallurgical industry, and, indeed, made it the subject of a Friday evening discourse at the Royal Institution. The writer well remembers assisting at the preparation of the experimental part of this lecture, and also making such analytical examinations as were required of the materials and products of the various stages of the process. The fact that the light of burning magnesium was highly actinic, and reacted powerfully upon sensitive silver salts, had been indicated by Bunsen and Roscoe, and Sir Henry Roscoe during his lecture demonstrated this property by actually taking a photograph of Faraday, who presided on the occasion. This, of course, was in the wet collodion days, when actinometers were unknown, and it was necessary to rehearse the demonstration with some care in order to determine the conditions of success. The late Prof. Schorlemmer and the writer were the first to submit themselves to the ordeal of being thus photographed, and Sonstadt, who was present, and who was greatly excited by the experiments, was the second, and his delight at its success was unbounded. He was at this time about thirty-five years of age: a frail, spare, thin-featured, highly-strung, sensitive man, with long flaxen hair, almost womanly in feature, save for the flowing beard and thin, wispy moustache.

In 1865 Sonstadt, whose health was at all times uncertain and precarious, and who, like the poet Cowley, was fond of a small house and a large garden, took up his residence at Port Levague, near Ramsey, in the Isle of Man. Here he fitted up a laboratory, and interested himself in the extraction of iodine from sea-water through the medium of kelp. At that time the iodine industry in North Britain, more particularly in the vicinity of Glasgow, was of considerable and of growing importance. It was, however, a highly speculative business, the price of iodine being subject to violent fluctuations, owing to market operations. Courtois, the discoverer of iodine, was ruined in the attempt to manufacture it, and died in poverty. Its commercial production in Great Britain was first tried by Dr. Ure, of Dictionary fame, and in 1845-46, tempted by the high price—31s. a pound—which then ruled, there were as many as twenty makers in Glasgow. In 1863 the price had temporarily fallen to 5s. a pound, and the manufacture was prac-

tically a monopoly, only two firms being engaged in it. At that time its method of production had been largely revolutionised by the late Mr. E. C. C. Stanford, who greatly improved the methods of collecting and treating the weed, so as to obviate in large measure the fluctuations in quality and yield arising from the uncertain climate of Scotland. The amount of kelp brought into the Clyde had risen from about 8000 tons in 1860 to 14,000 tons in 1863, with an upward tendency in the price of iodine, which steadily rose from 5s. per pound in 1863 to 34s. in 1872. Sonstadt began the manufacture of iodine about 1866, collecting the weed on the rocky shores stretching from Port Levague to Maughold Head. Here the conditions were very different from those prevailing in the Hebrides, where the peasantry had been kelp burners since the middle of the eighteenth century, and from the outset he met with many difficulties and much discouragement. Many of these difficulties he overcame, but no sooner was he in a position to place any considerable quantity of iodine on the market than the Scotch producers lowered their prices to a point at which competition became impossible, and the Manx venture, ill-starred from the beginning, collapsed, and Sonstadt well-nigh shared the fate of the unfortunate Courtois. With a resolution and self-denial characteristic of him, he set himself to retrieve the fallen fortunes of the company, and eventually managed to discharge all his liabilities and repay those who had participated in his luckless undertaking. But even if he had succeeded, his success could only, in the nature of things, have been temporary. As the sequel has shown, British iodine has been practically superseded by that obtained from *caliche*, which is capable of yielding far more than the world requires or is likely to require. The writer at this period was a constant visitor to Ramsey, and was personally witness of this attempt to establish the iodine industry in the island. To Sonstadt is due the credit of first drawing attention to the fact that iodine exists in sea-water, not as an iodide as generally supposed, but as an iodate and probably as calcium iodate; and he well remembers that fact being demonstrated to him in the little laboratory of which mention has been made. Sonstadt published some notes on the subject in the *Chemical News* for 1872. In the same year he also pointed out the existence of gold in sea-water. He published further a short paper on the existence of cæsium and rubidium in sea-water and in marine products. He was an extremely painstaking and accurate worker, thoroughly trustworthy, and scrupulously careful both in observation and inference.

In 1874 Sonstadt returned to London, and in the following year became chemist to a firm of chemical brokers, with whom he

remained until 1890, when, on the reconstruction of the firm after the death of one of the partners, he was retired. During his connexion with the firm he greatly improved the methods of testing anthracene, and was recognised as an expert on this subject. For many years he was an outside abstractor for the Patent Office, and had been promised an inside examinership, but failed in securing the position owing to the retrospective operation of an age limit. He was an abstractor for the Society of Chemical Industry from 1893 to the time of his death. For the last fifteen years of his life he lived very quietly at Cheshunt, latterly in comparatively comfortable circumstances owing to the unexpected improvement in certain small investments in which he was interested. He died in the eightieth year of his age, on July 5th, 1908.

T. E. THORPE.

THOMAS STEVENSON.

BORN APRIL 14TH, 1838; DIED JULY 27TH, 1908.

SIR THOMAS STEVENSON, who was the son of Mr. Peter Stevenson, a well-known landed proprietor and farmer, was born on April 14th, 1838, at Rainton, a village in the North Riding of Yorkshire. The family was an ancient one in Rainton, the very first entry in the Tipliffe Register—the parish in which Rainton is situated—being the marriage of one of the Stevensons.

Stevenson was educated at Tipliffe Grammar School, and remained there until he was nearly fifteen years of age; this school was provided with a laboratory, and he here acquired a rudimentary knowledge of chemistry sufficient to enable him to make rough analyses of soils and manures for his father. In 1853, he was sent to London, and continued his studies at Messrs. Nesbit's Chemical School in Kennington Lane, in the South of London. Professor Odling, A. H. Allen, of Sheffield, and Charles Graham were also pupils at this school, Graham being Stevenson's "chum." In 1855-6 he applied himself to the study of scientific agriculture on his father's farm, but later on, in 1857, he finally decided to adopt medicine rather than farming as his profession, and became a pupil of Mr. John Steel, of Bradford, with whom he studied for a time. In 1859, however, he left Bradford to come to the Capital, and here he matriculated at London University, and entered as a student at the Medical School of Guy's Hospital, with which in after years he became so

intimately associated. He was a most brilliant and most successful student, for in 1860 and again in 1862 he was First Prizeman of his Hospital, and in the latter year he obtained the much-coveted "Treasurer's Gold Medal" in Medicine. In 1861 he took the Scholarship in Chemistry at the First M.B. Examination at London University, also the second Gold Medal, and was classed the third place in Physiology. In 1862 he became a Member of the Royal College of Surgeons and Licentiate of the Royal College of Physicians, taking the Membership of the latter in 1864 and the Fellowship in 1871.

The year after he had qualified, that is, in 1863, he commenced practice at Bradford, but six months afterwards he returned to London, and in the same year graduated M.B. at the University, taking the Scholarship in Forensic Medicine, and the third place on the lists both in Surgery and in Medicine. In 1864 he graduated M.D. London.

In 1868 he became Medical Officer of Health to St. Pancras, Middlesex, an appointment which he held until 1878. In 1873 he was appointed Public Analyst, not only for the Borough of St. Pancras, but also for the Counties of Surrey and Bedford.

It was in 1872 that he was first asked to undertake analytical work for the Home Office, but it was not until some ten years afterwards, in 1882, that he was definitely appointed Senior Scientific Analyst to that Department. His name subsequently became associated with most of the great cases in toxicology in England, and in 1904 the King bestowed on him the honour of knighthood in recognition of his services to the State in that capacity.

In connexion with Guy's Hospital, he was appointed Demonstrator of Chemistry in 1864, and in 1870 Lecturer in Chemistry conjointly with Dr. Debus, Dr. Odling having retired and gone to Oxford as Professor of Chemistry there. In 1878 he succeeded Dr. Alfred Swayne Taylor as Lecturer in Forensic Medicine and Medical Jurisprudence.

Stevenson was elected a Fellow of the Chemical Society, forty-five years ago, in 1864, and served four times on the Council, once as a Vice-President. He was one of the founders of the Institute of Chemistry, of which he subsequently became President (1897-1900); he also conducted their first Examination in Pharmacology and Therapeutics. It was during his Presidency that the late Lord Brampton (Mr. Justice Hawkins) said of him, "He is a man who in giving evidence before me has always convinced me that he was right, and that it was useless to oppose him. I have admired him for his intelligence and knowledge, and respect him for his courage, candidness, and truth."

Sir Thomas was amongst those who founded the Society of Public Analysts, and was the first Treasurer of that Society, becoming President in 1896.

His contributions to chemical literature, which consisted mainly of papers on toxicology and analytical methods, were published in *Guy's Hospital Reports* and *The Analyst*.

In 1867 he married Miss Agnes Moberly, by whom he had seven children, namely, two sons and five daughters. Of the two sons, the younger, Claude, survives him and is in practice as a doctor at Cambridge; but the elder, his firstborn, was drowned at Whitby in August, 1895; this sad event is very pathetic, as his father had been instrumental in saving the lives of a number of people (nearly thirty) by the protracted use of artificial respiration after they had been brought out of the water insensible. One of the daughters has greatly distinguished herself in the medical profession, being M.D.Lond., B.S., and Gold Medallist in Surgery. She is now a sister in the Oxford Mission at Calcutta.

Stevenson's was a most estimable character, upright and truthful. He was ever kind and courteous, and always ready to help. Both he and Lady Stevenson were imbued with deep religious feeling, which was not apparent to those who were only casually acquainted with them. They both unostentatiously did lasting philanthropic work in the neighbourhood in which they lived.

The death of Lady Stevenson, which took place in January 17th, 1908, was a blow from which he never recovered, for they were deeply attached to one another. A great change came over him, he seemed suddenly to grow old, and, at the age of seventy, passed away on July 27th, six months after the death of his wife. He left many friends, who mourn his loss.

C. E. G.

The Council has ordered the following letter and report to be printed in the Journal and Proceedings of the Society :

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON,
LONDON, S.W.
November 17th, 1909.

GENTLEMEN,

I beg to present to the Council of the Chemical Society the Report of the International Committee on Atomic Weights, 1910, to which I have affixed, as desired by them, the signatures of Professors Ostwald and Urbain.

Since the Committee last reported, new determinations have been made of the atomic weights of chlorine, nitrogen, carbon, iodine, silver, phosphorus, arsenic, chromium, tellurium, mercury, palladium, krypton, and xenon.

Certain of the numbers obtained, if confirmed, would necessitate minor alterations in the tables, but as additional determinations are promised we prefer to make no very great changes until corroborative evidence is forthcoming. We suggest, however, that the value of Cr should be 52.0 ; that of As should be changed to 74.96 ; and we adopt the new values for krypton and xenon.

I am, Gentlemen,

Your obedient Servant,

T. E. THORPE.

*The Hon. Secretaries,
The Chemical Society,
Burlington House,
London, W.*

Report of the International Committee of Atomic Weights, 1910.

Since the preparation of our last report there has been much activity in the determination of atomic weights. A brief summary of the results obtained is as follows :

Chlorine.—A novel comparison of chlorine with oxygen is due to Guye and Fluss (*J. Chim. Phys.*, 1908, 6, 732). Nitrosyl chloride, NOCl, was first weighed, and then distilled over silver to absorb chlorine, then over heated copper to absorb oxygen, and finally over

metallic calcium, which retained the nitrogen. The complete analysis of the chloride was thus effected. From the direct weights of the oxygen and chlorine, $\text{Cl} = 35.468$.

Nitrogen.—In the investigation just cited, Guye and Fluss give data which correspond to $\text{N} = 14.006$. Guye and Pintza (*Compt. rend.*, 1908, 147, 925) determined the density of the mixed gases produced by the decomposition of ammonia, and so measured its composition by volume. If $\text{H} = 1.0076$, then $\text{N} = 14.014$. The authors regard the determination as having only a significance corroborative of the lower value for nitrogen.

The ratio $\text{AgCl} : \text{NH}_4\text{Cl} :: 100 : 37.3217$ has been measured by Richards, Koethner, and Tiede (*J. Amer. Chem. Soc.*, 1909, 31, 6). Reduced with $\text{Ag} = 107.881$, $\text{Cl} = 35.4574$, and $\text{H} = 1.0076$, $\text{N} = 14.0085$. If $\text{H} = 1.0078$, $\text{N} = 14.008$. The values assigned to silver and chlorine are derived from former researches by Richards and his colleagues in the Harvard laboratory.

Carbon.—From the ratio between silver and tetraethylammonium bromide, as measured by Scott (*Trans.*, 1909, 95, 1200), $\text{C} = 12.017$ when $\text{Ag} = 107.88$. A single experiment with the corresponding methyl compound gave $\text{C} = 12.019$. These values are too high to be accepted until they have been confirmed by other methods.

From the density of methane, Baume and Perrot (*Compt. rend.*, 1909, 148, 39) find $\text{C} = 12.004$. From the density of toluene, as determined by Ramsay and Steele, Leduc (*Compt. rend.*, 1909, 148, 832) computes $\text{C} = 12.003$.

Iodine and Silver.—Baxter and Tilley (*J. Amer. Chem. Soc.*, 1909, 31, 201) have determined the ratio between iodine pentoxide and silver. The pentoxide was reduced by means of hydrazine, and the hydriodic acid so produced was balanced in the usual way against silver. From the ratio thus found, $\text{I}_2\text{O}_5 : 2\text{Ag} :: 100 : 64.6225$ and 64.6230 (two series), combined with the ratio $\text{I} : \text{Ag} :: 100 : 84.8843$, the authors find that the atomic weight of Ag lies between 107.847 and 107.850. The corresponding value for iodine is $\text{I} = 126.891$.

Phosphorus.—From the density of phosphine, PH_3 , Ter Gazarian (*Compt. rend.*, 1909, 148, 1397) finds $\text{P} = 30.906$.

Arsenic.—Atomic weight redetermined by Baxter and Coffin (*J. Amer. Chem. Soc.*, 1909, 31, 297). The ratios $\text{Ag}_3\text{AsO}_4 : 3\text{AgCl}$ and $\text{Ag}_3\text{AsO}_4 : 3\text{AgBr}$ were determined by two methods, one by solution and precipitation in the usual way, the other by heating the arsenate in a stream of hydrochloric or hydrobromic acid. The final mean result is $\text{As} = 74.957$ when $\text{Ag} = 107.880$.

Chromium.—From analyses of silver chromate by two methods, Baxter, Mueller, and Hines (*J. Amer. Chem. Soc.*, 1909, 31, 529) find $\text{Cr} = 52.008$ when $\text{Ag} = 107.88$. With similar analyses of silver

dichromate, Baxter and Jesse (*J. Amer. Chem. Soc.*, 1909, **31**, 541) find $\text{Cr} = 52.013$. The mean value is 52.01.

Tellurium.—Lenher (*J. Amer. Chem. Soc.*, 1909, **31**, 20) converted the double bromide K_2TeBr_6 into 2KCl by heating, first in a stream of chlorine, and afterwards in hydrochloric acid. Sixteen very concordant experiments were made, giving the molecular ratio between the two compounds. The final mean value is $\text{Te} = 127.55$.

Mercury.—Analyses of mercuric chloride have been made by Easley,* who determined the proportion of mercury in the compound, and also the ratio $\text{HgCl}_2 : 2\text{AgCl}$. By the first method, $\text{Hg} = 200.48$; by the second method, $\text{Hg} = 200.62$. These values are surprisingly high; but as Easley is to continue his investigation, it would be unwise to accept them until his work is all done. It is quite possible that the increase may be ultimately verified.

Palladium.—Atomic weight determined by Gutbier, Haas, and Gebhardt † by analyses of palladosammine bromide. The final most probable mean value when $\text{N}_2\text{H}_6\text{r}_2 = \text{B}193.908$ is $\text{Pd} = 106.689$.

Krypton and Xenon.—Moore (*Trans.*, 1908, **93**, 2181) isolated krypton and xenon in considerable quantities from the residues from 120 tons of liquid air. Calculated from the densities of the two gases, the atomic weights are $\text{Kr} = 83.012$ and $\text{Xe} = 130.70$.

It will be seen from the evidence given above that few changes are needed in the table of atomic weights. Chromium, 52.01, may be rounded off to 52, as compared with the 52.1 formerly accepted. Arsenic becomes 74.96, in accordance with the work of Baxter and Coffin. The new values for krypton and xenon should also be adopted. As regards mercury, action may be deferred until more evidence is received.

F. W. CLARKE.
W. OSTWALD.
T. E. THORPE.
G. URBAIN.

* *Private communication*. Easley's work is soon to be published.

† *J. pr. Chem.*, 1909, [ii], **79**, 457. This includes the work of Haas, cited in the Report for 1909.

1910.

International Atomic Weights.

		O = 16.			O = 16.
Aluminium	Al	27·1	Molybdenum	Mo	96·0
Antimony	Sb	120·2	Neodymium	Nd	144·3
Argon	A	39·9	Neon	Ne	20·0
Arsenic	As	74·96	Nickel	Ni	58·68
Barium	Ba	137·37	Nitrogen	N	14·01
Bismuth	Bi	208·0	Osmium	Os	190·9
Boron	B	11·0	Oxygen	O	16·00
Bromine	Br	79·92	Palladium	Pd	106·7
Cadmium	Cd	112·40	Phosphorus	P	31·0
Cæsium	Cs	132·81	Platinum	Pt	195·0
Calcium	Ca	40·09	Potassium	K	39·10
Carbon	C	12·00	Praseodymium	Pr	140·6
Cerium	Ce	140·25	Radium	Ra	226·4
Chlorine	Cl	35·46	Rhodium	Rh	102·9
Chromium	Cr	52·0	Rubidium	Rb	85·45
Cobalt	Co	58·97	Ruthenium	Ru	101·7
Columbium	Cb	93·5	Samarium	Sa	150·4
Copper	Cu	63·57	Scandium	Sc	44·1
Dysprosium	Dy	162·5	Selenium	Se	79·2
Erbium	Er	167·4	Silicon	Si	28·3
Europium	Eu	152·0	Silver	Ag	107·88
Fluorine	F	19·0	Sodium	Na	23·00
Gadolinium	Gd	157·3	Strontium	Sr	87·62
Gallium	Ga	69·9	Sulphur	S	32·07
Germanium	Ge	72·5	Tantalum	Ta	181·0
Glucium	Gl	9·1	Tellurium	Te	127·5
Gold	Au	197·2	Terbium	Tb	159·2
Helium	He	4·0	Thallium	Tl	204·0
Hydrogen	H	1·008	Thorium	Th	232·42
Indium	In	114·8	Thulium	Tm	168·5
Iodine	I	126·92	Tin	Sn	119·0
Iridium	Ir	193·1	Titanium	Ti	48·1
Iron	Fe	55·85	Tungsten	W	184·0
Krypton	Kr	83·0	Uranium	U	238·5
Lanthanum	La	139·0	Vanadium	V	51·2
Lead	Pb	207·10	Xenon	Xe	130·7
Lithium	Li	7·00	Ytterbium (Neoytterbium)	Yb	172·0
Lutecium	Lu	174·0	Yttrium	Y	89·0
Magnesium	Mg	24·32	Zinc	Zn	65·37
Manganese	Mn	54·93	Zirconium	Zr	90·6
Mercury	Hg	200·0			

INDEX OF AUTHORS' NAMES.

TRANSACTIONS AND PROCEEDINGS. 1909.

(Marked T. and P. respectively.)

A.

- Agnew, James Watson.** See *George Gerald Henderson.*
- Alcock, (Miss) Mary.** See *Gilbert Thomas Morgan.*
- Allmand, Arthur John,** the electromotive behaviour of cuprous oxide and cupric hydroxide in alkaline electrolytes, T., 2151; P., 258.
- Anderson, (Miss) Emma Alexander.** See *John Kerfoot Wood.*
- Auld, Samuel James Manson,** the hydrolysis of amygdalin by emulsin. Part III. Synthesis of *d*-benzaldehyde-cyanohydrin, T., 927; P., 62.
an examination of irritant woods. Part I. Chloroxytonine from East Indian satinwood, T., 964; P., 148.

B.

- Bain, (Miss) Alice Mary.** See *William Hobson Mills.*
- Baker, (Miss) Sarah Martha,** a theory regarding the configuration of certain unsaturated compounds; and its application to the metallic amines and the cinnamic acids, P., 223.
- Ball, Walter Craven,** slow decomposition of ammonium chromate, dichromate, and trichromate by heat, T., 87.
a new method for the detection of sodium, cesium, and rubidium, T., 2126; P., 284; discussion P., 284.
- Baly, Edward Charles Cyril, (Miss) Katherine Alice Burke,** and *(Miss) Effie Gwendoline Marsden,* the absorption spectra of the nitrates in relation to the ionic theory, T., 1096; P., 144; discussion, P., 145.

- Baly, Edward Charles Cyril, John Norman Collie,** and *Herbert Edmeston Watson,* relation between absorption spectra and chemical constitution. Part XIII. Some pyrones and allied compounds, T., 144.
- Banerjee, S. C.** See *George Clarke, jun.*
- Barger, George,** isolation and synthesis of *p*-hydroxyphenylethylamine, an active principle of ergot soluble in water, T., 1123; P., 162.
synthesis of hordenine, the alkaloid from barley, T., 2193; P., 289.
- Barger, George,** and *Arthur James Ewins,* the action of phosphorus pentachloride on the methylene ethers of catechol derivatives. Part IV. Derivatives of dihydroxyphenyl-acetic, -glycollic, and -glyoxylic acids, T., 552; P., 86.
- Barger, George,** and *George Stanley Walpole,* further syntheses of *p*-hydroxyphenylethylamine, T., 1720; P., 229.
- Barnett, Edward de Barry,** the action of hydrogen dioxide on thiocarbamides, P., 305.
- Barnett, Edward de Barry,** and *Samuel Smiles,* the intramolecular rearrangement of diphenylamine ortho-sulphoxides, T., 1253; P., 195.
intramolecular rearrangement of the diphenylamine sulphoxides; preliminary note, P., 74.
- Barrett, William Henry.** See *Harold Hartley.*
- Barrow, Fred.** See *Percy Faraday Frankland.*
- Barrowcliff, Marmaduke,** and *Frank Tutin,* the configuration of tropine and ψ -tropine and the resolution of atropine, T., 1966; P., 256; discussion, P., 257.

- Baudisch, Oscar, Gilbert Stanley Hibbert, and William Henry Perkin, jun.**, the reduction of 4-hydroxy-*o*-toluic acid, T., 1870; P., 249.
- Baudisch, Oscar, and William Henry Perkin, jun.**, the reduction of 6-hydroxy-*o*-toluic acid, T., 1883; P., 249.
- Best, Stanley Robert, and Jocelyn Field Thorpe**, the formation and reactions of imino-compounds. Part VII. The formation of 1:3-naphthylenediamine from β -in.ino- α -cyano- γ -phenylpropane, T., 8.
- the formation and reactions of imino-compounds. Part VIII. The formation of methyl derivatives of 2-phenyl-1:3-naphthylenediamine from the three tolylacetonitriles, T., 261; P., 28.
- the formation and reactions of imino-compounds. Part IX. The formation of derivatives of cyclopentane from $\alpha\delta$ -dicyano-derivatives of butane, T., 685; P., 92.
- the formation and reactions of imino-compounds. Part X. The formation of imino-derivatives of pyrrole and of isopyrrole from amino-nitriles, T., 1506; P., 216.
- Bloxam, William Popplewell.** See *Frederick Thomas*.
- Boyd, David Runciman, and Herbert Stanley Knowlton**, the action of ammonia on the glycide aryl ethers. Part I. *o*-Tolyloxypropanolamines, T., 1802; P., 235.
- Boyd, David Runciman, and Ernest Robert Marle**, the action of potassium hydroxide on epichlorohydrin in presence of monohydric phenols, T., 1807; P., 235.
- Boyle, (Miss) Mary**, the iodobenzene-monosulphonic acids. Part I, T., 1683; P., 35.
- Brough, Bennett Hooper**, obituary notice of, T., 2202.
- Burke, (Miss) Katherine Alice.** See *Edward Charles Cyril Baly*.
- Burt, Frank Playfair.** See *Robert Whyllaw Gray*.
- Buttle, Bertram Harvard, and John Theodore Hewitt**, the constitution of polynitrophenols in alkaline solution, T., 1755; P., 231.
- C.**
- Cahen, Edward.** See *Harry Frank Victor Little*.
- Cain, John Cannell**, nitrosoacetylaminoderivatives of the benzene and diphenyl series, T., 714; P., 123
- 3-nitrodurene, P., 260.
- Caldwell, Kenneth Somerville, and William Holdsworth Hurlley**, the distillation of butter fat, cocoanut oil, and their fatty acids, T., 853; P., 73.
- Cameron, William.** See *George Gerald Henderson*.
- Caton, Frederic William.** See *Frank Tutin*.
- Chapman, David Leonard, and Patrick Sarsfield MacMahon**, the interaction of hydrogen and chlorine, T., 135; P., 15.
- the retarding effect of oxygen on the rate of interaction of chlorine and hydrogen, T., 959; P., 148.
- the influence of gaseous oxides of nitrogen on the rate of interaction of chlorine and hydrogen, T., 1717; P., 224.
- Chapman, David Leonard, and Leonard Vodden**, nitrogen chloride, T., 138; P., 15.
- Chattaway, Frederick Daniel**, synthesis of para-urazine from carbamide, T., 235; P., 10.
- the preparation of dichlorocarbamide, T., 464; P., 72.
- the preparation and properties of the *N*-tribromo-substituted hydrazines (the diazonium perbromides), T., 862; P., 120.
- the action of the halogens on aromatic hydrazines, T., 1065; P., 147.
- ammonium perhalides, P., 163.
- Chattaway, Frederick Daniel, and Donald Frederick Sandys Wunsch**, chlorine derivatives of substituted carbamides, T., 129; P., 11.
- Clarke, Frank Wigglesworth**, Gibbs memorial lecture, T., 1299; P., 171.
- Clarke, George, jun., and S. C. Banerjee**, a glucoside from *Tephrosia purpurea*; preliminary note, P., 16.
- Clarke, Hans Thacher, and Samuel Smiles**, diethoxythioxan; a relation between the refractive power and chemical activity of some sulphur compounds, T., 992; P., 145; discussion, P., 146.
- Clarke, Reginald William Lane, and Arthur Lapworth**, cyanocarone, P., 307.
- Clewer, Hubert William Bentley.** See *Frank Tutin*.
- Clough, George William.** See *Alexander McKenzie*.
- Cobb, John W.**, the formation of silicates, glasses, and glazes, P., 165.
- Collie, John Norman.** See *Edward Charles Cyril Baly*.
- Compton, Arthur.** See *Alfred Senier*.

Coward, Hubert Frank. See *Harold Baily Dixon*.

Crossley, Arthur William, and Charles Gilling, hydroaromatic ketones. Part I. Synthesis of trimethylcyclohexenone (isophorone) and some homologues, T., 19.

note on the preparation of trimethylcyclohexenone (isophorone) from ethyl malonate and chlorodimethylcyclohexenone, P., 96.

Crossley, Arthur William, and Charles Herbert Hampshire, nitrotetramethyldiphenyl; preliminary note, P., 162.

Crossley, Arthur William, and (Miss) Nora Renouf, nitro-derivatives of ortho-xylene, T., 202; P., 26. substituted dihydrobenzenes. Part III. The so-called 1:1-dimethyl- $\Delta^{2:5}$ -cyclohexadiene of Harries and Antoni, T., 930; P., 145.

Cumming, Alexander Charles, a method for the measurement of vapour pressures, T., 1772; P., 237.

Cunningham, (Miss) Mary, and Frederick Mollwo Perkin, studies on the cobalt-nitrites, T., 1562.

D.

Dakin, Henry Drysdale, the oxidation of hydroxy-derivatives of benzaldehyde and acetophenone, P., 194.

Davis, Harold. See *Frederic Stanley Kipping*.

Davis, Morton James Pryce. See *John Joseph Sudborough*.

Davis, Oliver Charles Minty, the quantitative decomposition of the anilides: a study in steric influence, T., 1397; P., 197.

Davis, Oliver Charles Minty. See also *Francis Francis*.

Dawson, Harry Medforth, the nature of ammoniacal copper solutions. Part II. The solubility of cupric hydroxide in ammoniacal sulphate solutions, T., 370; P., 33.

a method for investigating dissociation equilibria in solutions, and its application to the study of aqueous potassium mercuri-iodide solutions, T., 870; P., 129.

Dawson, Harry Medforth, and (Miss) May Sybil Leslie, dynamics of the reaction between iodine and acetone, T., 1860; P., 246.

Denham, William Smith, the action of sulphur monochloride on salts of organic acids: a convenient method of preparing anhydrides, T., 1235; P., 179.

Denham, William Smith, preparation of anhydrides by the action of thionyl chloride on salts of organic acids; preliminary note, P., 294.

Desch, Cecil Henry. See *Thomas Martin Lowry*.

Dixon, Harold Baily, and Hubert Frank Coward, the ignition-temperatures of gases, T., 514; P., 67.

Dobson, (Miss) Mary Elizabeth, John Ferns, and William Henry Perkin, jun., synthesis of cyclohexanone-3-carboxylic acid, T., 2010; P., 263.

Donnan, Frederick George, and Wilhelm Schneider, the colour of aqueous solutions of violuric acid, T., 956; P., 148.

Dorée, Charles, contributions to the chemistry of cholesterol and coprosterol, T., 638; P., 88.

Dunlop, John Gunning Moore, and Humphrey Owen Jones, the action of ethylene dibromide on monomethylaniline, T., 416; P., 61.

Dunn, Frederick Percy. See *Martin Onslow Forster*.

Dunstan, Albert Ernest, and Ferdinand Bernard Thole, the relation between viscosity and chemical constitution. Part IV. Viscosity and hydration in solution, T., 1556; P., 219.

Dutta, Jatindra M. See *A. Chandra Sirkar and Edwin Roy Watson*.

E.

Eastburn, Wilfred James Stevenson. See *George Gerald Henderson*.

Edgerton, John Percy, a new method of preparing camphoric anhydride, P., 149.

Egerton, Alfred Charles Glyn, divergence of the atomic weights of the lighter elements from whole numbers, T., 233; P., 26.

Ewins, Arthur James, the action of phosphorus pentachloride on the methylene ethers of catechol derivatives. Part V. Derivatives of protocatechuyl alcohol and protocatechuonitrile, T., 1482; P., 210.

Ewins, Arthur James. See also *George Barger*.

F.

Fenton, Henry John Horstman, and Fred Robinson, homologues of furfuraldehyde, T., 1334; P., 193.

Fenton, Henry John Horstman, and William Arthur Reginald Wilks, isomiazolone, T., 1329; P., 192.

- Ferns, *John*. See (*Miss Mary Elizabeth Dobson*).
- Ferraboschi, *Frederic*, the oxidation of mucic acid in presence of iron, T., 1248; P., 178.
the production of ozone in the interaction between hydrogen dioxide and sulphur dioxide; preliminary note, P., 179.
- Fielding, *William*. See *John Norman Pring*.
- Findlay, *Alexander*, and (*Miss Evelyn Marion Hickmans*), the influence of hydroxy- and alkyloxy-groups on the velocity of saponification. Part II., T., 1004; P., 152.
the partial racemisation of menthyl *r*-mandelate, T., 1386; P., 196.
- Findlay, *Alexander*, *William Ernest Stephen Turner*, and (*Miss Gertrude Emily Owen*), affinity constants of hydroxy- and alkyloxy-acids, T., 938; P., 146.
- Finnemore, *Horace*, the constituents of Canadian hemp. Part II. Cynotoxin; preliminary note, P., 76.
- Finnemore, *Horace*. See also *John Wade*.
- Flaschner, *Otto*, the action of β -rays on photosensitive solutions, T., 327; P., 34.
the miscibility of the pyridine bases with water and the influence of a critical-solution point on the shape of the melting-point curve, T., 668; P., 71.
- Flürscheim, *Bernard*, the relation between the strength of acids and bases and the quantitative distribution of affinity in the molecule, T., 718; P., 22.
the mechanism of the reduction of nitroanilines and nitrophenols, P., 21.
the relation between the strengths of acids and bases, and the quantitative distribution of affinity in the molecule. Part II., P., 193.
chemical affinity and electrons; preliminary note, P., 261.
- Forster, *Martin Onslow*, the triazo-group. Part VII. Interaction of benzhydroxamic chloride and sodium azide, T., 184; P., 25.
the triazo-group. Part IX. Transformation of cinnamoylazoimide into cinnamylcarbimide (cinnamyl isocyanate), T., 433; P., 69.
- Forster, *Martin Onslow*, and *Frederick Percy Dunn*, an interpretation of the Hantzsch-Werner hypothesis, T., 425; P., 68.
- Forster, *Martin Onslow*, and *Charles Samuel Garland*, studies in the camphane series. Part XXVII. Camphorylphenyltriazine (camphordiazaminobenzene) and its bearing on the constitution of diazoamino-compounds, T., 2051; P., 244; discussion, P., 244.
- Forster, *Martin Onslow*, and *Robert Müller*, the triazo-group. Part VIII. Azoimides of the monobasic aliphatic acids, T., 191; P., 26.
the triazo-group. Part X. Triazoantipyrine, T., 2072; P., 291.
- Forster, *Martin Onslow*, and *Tom Thornley*, studies in the camphane series. Part XXVI. Aryl derivatives of iminocamphor, T., 942; P., 145; discussion, P., 145.
- Fox, *John Jacob*, solubility of lead sulphate in concentrated solutions of sodium and potassium acetates, T., 878; P., 128.
- Francis, *Francis*, and *Oliver Charles Minty Davis*, preparation of the acyl derivatives of the aldehyde-cyanohydrins. Part I., T., 1403; P., 210.
- Frankland, *Percy Faraday*, and *Fred Barrow*, the acyl-bornylamines. Part I. Fatty bornylamides, T., 2017; P., 263.
the acyl-bornylamines. Part II. Aromatic bornylamides, T., 2026; P., 263.
- Friend, *John Albert Newton*, estimation of iron by permanganate in the presence of hydrogen chloride, T., 1228; P., 150.
the action of steam on iron; preliminary note, P., 90.
the constitution of sulphurous, sulphuric, carbonic, and formic acids, P., 91.
estimation of small quantities of ferrous iron by potassium permanganate in the presence of hydrogen chloride, P., 224.
- Friswell, *Richard John*, obituary notice of, T., 2204.

G.

- Gardner, *Henry Dent, jun.*, and *Walter Norman Haworth*, the condensation of ketones and aldehydes with the sodium derivative of ethyl cyanoacetate, T., 1955; P., 250.
- Gardner, *Walter Myers*, and *Herbert Henry Hodgson*, the iodination of phenols and the iodometric estimation of, and action of reducing agents on, tannic acid, T., 1819.

- Garland, Charles Samuel.** See *Martin Onslow Forster*.
- Garner, Frederick Basil.** See *James Charles Philip*.
- Gebhard, Norman Leslie, and Herbert Bryan Thompson,** diazohydroxylamino-compounds and the influence of substituting groups on the stability of their molecules. Part I., T., 767; P., 70. Part II., T., 1115; P., 149.
- Gibbs, [Oliver] Wolcott,** memorial lecture on (CLARKE), T., 1299; P., 171.
- Gilling, Charles.** See *Arthur William Crossley*.
- Gilmour, Robert,** the mutarotation of glucose and its nitrogen derivative, P., 225.
- Gilmour, Robert.** See also *James Colquhoun Irvine*.
- Gittins, James Mylam.** See *John Joseph Sudborough*.
- Gortner, Ross Aiken,** a contribution to the study of the oxydases, P., 306.
- Gray, Francis William,** direct proofs of the presence of the hydroxyl group in derivatives of anhydroacetonebenzil, T., 2131; P., 218.
isomerides of anhydroacetonebenzil and its derivatives, T., 2138; P., 218.
- Gray, Robert Whytlaw, and Frank Playfair Burt,** the atomic weight of chlorine, T., 1633; P., 216.
- Gray, Robert Whytlaw, and (Sir) William Ramsay,** some physical properties of radium emanation, T., 1073; P., 161; discussion, P., 162.
liquid and solid radium emanation, P., 82.
- Gregory, Arnold William,** a colorimetric method for the estimation of small quantities of vanadium, P., 232.

H.

- Haas, Paul,** the condensation of dimethyldihydroresorcin with ethylamine, T., 421; P., 19.
- Hampshire, Charles Herbert.** See *Arthur William Crossley*.
- Hann, Archie Cecil Osborn.** See *Frank Tutin*.
- Hansen, Edward Kenneth,** phycoerythrin, the pigment of the red algae, P., 117; discussion, P., 117.
- Harrop, (Miss) Dorothy, Roland Victor Norris, and Charles Weizmann,** derivatives of naphthacenequinone. Part III., T., 279; P., 33.
some derivatives of anthraquinone, T., 1312; P., 203.
- Hartley, Harold, and William Henry Barrett,** sodium sulphite and its equilibrium with water, T., 1178; P., 164.
- Hartley, Walter Noel,** the constitution of para-benzoquinone, T., 52.
- Hartley, Walter Noel, and Alfred Godfrey Gordon Leonard,** the absorption spectra of para-benzoquinone, quinol, and quinhydrone in the state of vapour and in solution, T., 34.
- Haworth, Walter Norman,** the condensation of ketones and aldehydes with the sodium derivative of ethyl cyanoacetate, T., 480; P., 76.
- Haworth, Walter Norman.** See also *Henry Dent Gardner, jun.*
- Hay, James Gordon.** See *Raphael Meldola*.
- Henderson, George Gerald, and James Watson Agnew,** contributions to the chemistry of the terpenes. Part IV. The oxidation of pinene with mercuric acetate, T., 289; P., 35.
- Henderson, George Gerald, and William Cameron,** contributions to the chemistry of the terpenes. Part V. The action of chromyl chloride on terpinene and on limonene, T., 969; P., 151.
- Henderson, George Gerald, and Wilfred James Stevenson Eastburn,** the conversion of pinene into sobrerol, T., 1465; P., 211.
- Hewitt, John Theodore, Sidney Herbert Newman, and Thomas Field Winmill,** studies in the azine series. Part I. The constitution of safranine, T., 577; P., 86.
- Hewitt, John Theodore, and Ferdinand Bernard Thole,** the colour and constitution of azo-compounds. Part IV., T., 1393; P., 208.
- Hewitt, John Theodore, and William Thomas,** the colour and constitution of azo-compounds. Part III., T., 1292; P., 190.
- Hewitt, John Theodore.** See also *Bertram Howard Buttle*.
- Hibbert, (Miss) Eva.** See *Edmund Knecht*.
- Hibbert, Gilbert Stanley.** See *Oscar Baudisch*.
- Hibbert, Harold,** the estimation of hydroxyl derivatives in mixtures of organic compounds, P., 57.
a simple method for determining the chemical affinity of organic substances, P., 57; discussion, P., 58.
the stability of compounds derived from tertiary amines and magnesium alkyl halides, P., 118.

- Hibbert, Harold, and Archibald Wise**, a new method for the separation of tertiary from secondary and primary amines, P., 119.
- Hibbert, Harold.** See also *John Joseph Sudborough*.
- Hickmans, (Miss) Evelyn Marion.** See *Alexander Findlay*.
- Hicks, William Longton.** See *Arthur Walsh Titherley*.
- Hilditch, Thomas Percy**, the effect of contiguous unsaturated groups on optical activity. Part I., T., 331; P., 29.
- the effect of contiguous unsaturated groups on optical activity. Part II. Acids containing two adjacent ethlenoid groups, T., 1570; P., 214.
- the effect of contiguous unsaturated groups on optical activity. Part III. The normal series of fatty dibasic acids, T., 1578; P., 214.
- Hodgson, Herbert Henry.** See *Walter Myers Gardner*.
- Holmes, John, and Philip John Sageman**, contributions to the theory of solutions, T., 1919; P., 231.
- Holt, Alfred, jun.**, the decomposition of carbon dioxide by the silent electric discharge, T., 30.
- Hope, Edward, and William Henry Perkin, jun.**, the action of bromocyclohexane and of 4-bromo-1-methylcyclohexane on the sodium derivative of ethyl malonate, T., 1360; P., 207.
- ethyl benzoylacetate, T., 2042; P., 296.
- Howard, Hubert.** See *Frank George Pope*.
- Humphries, Herbert Brooke Perren.** See *Alexander McKenzie*.
- Hurtley, William Holdsworth.** See *Kenneth Somerville Caldwell*.
- Hynd, Alexander.** See *James Colquhoun Irvine*.

I.

- Inglis, John Kenneth Harold, and Alfred Sidell Mason**, action of Grignard's reagent on ethyl oxalate, P., 195.
- Irvine, James Colquhoun**, a polarimetric method of identifying chitin, T., 564; P., 89.
- Irvine, James Colquhoun, and Robert Gilmour**, the constitution of glucose derivatives. Part II. Condensation derivatives of glucose with aromatic amino-compounds, T., 1545; P., 218.

- Irvine, James Colquhoun, and Alexander Hynd**, monomethyl levulose and its derivatives: constitution of levulose-diacetone, T., 1220; P., 176.
- Isherwood, Percy Claude Cameron**, the coloured salts and derivatives of the thioviolic acid group; preliminary note, P., 120.

J.

- Jackson, (Miss) Kate Maul, and Henry Allen Dugdale Neville**, substituted amides of tartaric acid, P., 226.
- James, Thomas Campbell, and John Joseph Sudborough**, halogen derivatives of cinnamic acid, T., 1538; P., 211.
- Jerusalem, George**, the morphotropic relationships between the derivatives of picric acid, T., 1275; P., 201.
- Jones, Bernard Mouat**, the spontaneous crystallisation of solutions of sodium carbonate and sodium thiosulphate, T., 1672; P., 213.
- Jones, Humphrey Owen, and Hubert Sanderson Tasker**, the action of mercaptans on acid chlorides. Part I. Oxalyl chloride: the mono- and dithio-oxalates, T., 1904; P., 247.
- thio-oxalates; preliminary note, P., 159.
- Jones, Humphrey Owen.** See also *John Gunning Moore Dunlop, and Hubert Sanderson Tasker*.
- Jones, Lionel Manfred.** See *Thomas Slater Price*.
- Jones, William Jacob, and Kennedy Joseph Previté Orton**, the chlorination of acetanilide, T., 1056; P., 146.
- Jones, William Jacob.** See also *Kennedy Joseph Previté Orton*.
- Jowett, Hooper Albert Dickinson, and Frank Lee Pyman**, relation between chemical constitution and physiological action in the tropelines. Part II., T., 1020; P., 165.

K.

- Kametaka, T., and Arthur George Perkin**, carthamine; preliminary note, P., 223.
- Kay, Francis William**, the conversion of *d*- α -methylisoserine into *d*- α -methylglyceric acid, T., 560; P., 90.
- Kenyon, Joseph.** See *Robert Howson Pickard*.
- Kipping, Frederic Stanley**, a study of some asymmetric compounds, T., 408; P., 55.

- Kipping, Frederic Stanley, and Harold Davis**, organic derivatives of silicon. Part IX. Experiments on the resolution of *dl*-benzylethylpropylisobutylsilicanesulphonic acid, T., 69; P., 9.
- Kipping, Frederic Stanley, and Bernard Dunstan Wilkinson Luff**, isomeric derivatives of phosphoric acid, P., 203.
- Kipping, Frederic Stanley, and Geoffrey Martin**, the action of fuming sulphuric acid on triphenylsilicol, T., 489; P., 66.
- Kipping, Frederic Stanley, and William Jackson Pope**, crystallisation of externally compensated mixtures, T., 103; P., 9.
- Kipping, Frederic Stanley**. See also **Bernard Dunstan Wilkinson Luff, Geoffrey Martin, and Arthur Henry Salway**.
- Knecht, Edmund**, the reduction of perchlorates by titanous salts, P., 229.
- Knecht, Edmund, and (Miss) Eva Hibbert**, a volumetric process for the estimation of tungsten, P., 227.
- Knowlton, Herbert Stanley**. See **David Runciman Boyd**.
- Knox, Joseph**, the solubility of bismuth trisulphide in alkali sulphides and of bismuth trioxide in alkali hydroxides, T., 1760; P., 226.
the volumetric estimation of mercury and the estimation of silver in presence of mercury, T., 1768; P., 227.
- Krieble, Vernon K.** See **James Wallace Walker**.
- L.**
- Laplough, Francis Edward Everard**, note on the determination of the rate of chemical change by measurement of the gases evolved, P., 23; discussion, P., 24.
the determination of the rate of decomposition of benzenediazonium chloride, P., 166.
- Lang, William Robert, and John Obins Woodhouse**, some esters of arsenic acid. Part II. Resorciny arsenite, P., 199.
- Lapworth, Arthur**, note on the variation in the catalytic activity of mineral acids with changes in their concentration, P., 19.
- Lapworth, Arthur, and James Riddick Partington**, the influence of water on the availability of hydrogen chloride in alcoholic solution, P., 307.
- Lapworth, Arthur, and Elkan Wechsler**, experiments on substituted allene-carboxylic acids. Part I., P., 307.
- Lapworth, Arthur**. See also **Reginald William Lane Clarke**.
- Leonard, Alfred Godfrey Gordon**. See **Walter Noel Hartley**.
- Leslie, (Miss) May Sybil**. See **Harry Melforth Dawson**.
- Le Sueur, Henry Rondel**, formation of heterocyclic compounds. Part I. 1-Phenylpyrrolidine-2 : 5-dicarboxylic acid from adipic acid, T., 273; P., 36.
- Lewis, Samuel Judd**. See **Edgar Wedekind**.
- Lewis, William Culmore McCullagh**, adsorption in relation to Gibbs's theory: the mercury adsorbing surface, P., 258; discussion, P., 258.
- Little, Harry Frank Victor, Edward Cahen, and Gilbert Thomas Morgan**, the estimation of arsenic in organic compounds, T., 1477; P., 212.
- Lloyd, Percy Vivian**. See **Clarence Arthur Seyler**.
- Lowry, Thomas Martin, and Cecil Henry Desch**, studies of dynamic isomerism. Part VIII. The relationship between absorption spectra and isomeric change. Absorption spectra of halogen, nitro-, and methyl derivatives of camphor, T., 807; P., 13. studies of dynamic isomerism. Part IX. The relationship between absorption spectra and isomeric change. Absorption spectra of sulphonic derivatives of camphor, T., 1840; P., 192.
- Luff, Bernard Dunstan Wilkinson, and Frederic Stanley Kipping**, the resolution of asymmetrical derivatives of phosphoric acid, T., 1993; P., 256.
- Luff, Bernard Dunstan Wilkinson**. See also **Frederic Stanley Kipping**.
- M.**
- McCombie, Hamilton, and (Miss) Ethel Parry**, condensations of cyanohydrins. Part I. Condensation products from anisaldehyde cyanohydrin and cinnamaldehyde cyanohydrin, T., 584; P., 95.
- McDonald, David Paterson**. See **Thomas Stewart Patterson**.
- McKenzie, Alexander, and George William Clough**, experiments on the Walden inversion. Part II. The interconversion of the optically active mandelic acids, T., 777; P., 70.
- McKenzie, Alexander, and Herbert Brooke Perren Humphries**, studies in asymmetric synthesis. Part VIII. The asymmetric synthesis of *l*-mandelic acid, T., 1105; P., 164.

- McKenzie, *Alexander*, and *Hermann August Müller*, studies in asymmetric synthesis. Part VII. The influence of the *d*-amyl group, T., 544; P., 88.
- MacKey, *John Francis*, some esters of anti-ony trioxide, T., 604; P., 98.
- MacMahon, *Patrick Sarsfield*. See *David Leonard Chapman*.
- Marle, *Ernest Robert*, the estimation of carbonates in presence of nitrites, sulphides, or sulphites by means of potassium dichromate, T., 1491; P., 154.
the action of carbon dioxide on nitrites, P., 74.
- Marle, *Ernest Robert*. See also *David Runciman Boyd*.
- Marsden, (*Miss*) *Effie Gwendoline*. See *Edward Charles Cyril Baly*.
- Marsh, *James Ernest*, and *Robert de Jersey Fleming Struthers*, some mercury derivatives of camphor, T., 1777; P., 228.
- Martin, *Geoffrey*, and *Frederic Stanley Kipping*, benzyl and ethyl derivatives of silicon tetrachloride, T., 302; P., 27.
- Martin, *Geoffrey*. See also *Frederic Stanley Kipping*.
- Mason, *Alfred Sidell*. See *John Kenneth Harold Inglis*.
- Meldola, *Raphael*, and *James Gordon Hay*, syntheses with phenol derivatives containing a mobile nitro-group. Part II. The interaction of 2:3:5-trinitro-4-acetylaminophenol and amines (continued), T., 1033; P., 167.
2:3:5-trinitro-4-aminophenol and derivatives, T., 1378; P., 207.
- Meldrum, *Andrew Norman*, and *William Henry Perkin, jun.*, the reduction of 5-hydroxy-*m*-toluic acid, T., 1889; P., 249.
- Mendeléeff, *Dmitri Ivanovitch*, memorial lecture on (TILDEN), T., 2077.
- Merriman, *Richard William*. See *John Wade*.
- Micklethwait, (*Miss*) *Frances Mary Gore*. See *Gilbert Thomas Morgan*.
- Mills, *William Hobson*, and (*Miss*) *Alice Mary Bain*, optically active 4-oximino-cyclohexanecarboxylic acid and the configuration of the oximino-group; preliminary note, P., 177.
- Mitchell, *Alec Duncan*, and *Clarence Smith*, constitution of hydroxyazo-compounds. Part II. Action of mercuric acetate on benzeneazomaphthols, T., 1430; P., 209.
volumetric estimation of sulphates, T., 2198; P., 291.
- Moir, *James*, a method of harmonising the atomic weights, T., 1752; P., 213.
- Montgomerie, *Harvey Hugh*. See *Thomas Stewart Patterson*.
- Moody, *Gerald Tattersall*, the rusting of iron, P., 34.
- Moore, *Charles Watson*, the constituents of the rhizome of *Apocynum androsaemifolium*, T., 734; P., 85.
- Moore, *Charles Watson*. See also *Frederick Belding Power*.
- Moore, *Tom Sidney*. See *Neril Vincent Sidgwick*.
- Moore, *William Roman*. See *Gilbert Thomas Morgan*.
- Morgan, *Gilbert Thomas*, and (*Miss*) *Mary Alcock*, the colour and constitution of diazonium salts. Part I, T., 1319; P., 202.
- Morgan, *Gilbert Thomas*, and (*Miss*) *Frances Mary Gore Micklethwait*, organic derivatives of arsenic. Part II. Triaminotriphenylarsine oxide and triamphorylarsinic acid, T., 1473; P., 212.
- Morgan, *Gilbert Thomas*, (*Miss*) *Frances Mary Gore Micklethwait*, and *George Stafford Whitby*, organic derivatives of antimony. Part I. Triamphorylstibine chloride and triphenylstibine hydroxynitrate and hydroxysulphate, P., 302.
- Morgan, *Gilbert Thomas*, and *William Roman Moore*, dicamphorylphosphinic acid, P., 310.
- Morgan, *Gilbert Thomas*, and *Joseph Allen Pickard*, the production of para-diazoimides from alkyl- and arylsulphonyl-para-diamines. A general reaction, P., 300; discussion, P., 301.
- Morgan, *Gilbert Thomas*. See also *Harry Frank Victor Little*.
- Mouilpied, *Alfred Theophilus de*, and *Alexander Rule*, tetraketopiperazine. Part II., T., 549; P., 71.
- Mountain, *Harold*. See (*Miss*) *Martha Annie Whiteley*.
- Müller, *Hermann August*. See *Alexander McKenzie*.
- Müller, *Robert*. See *Martin Onslow Forster*.
- Muir, *Matthew Monerieff Pattison*, iodine dioxide, T., 656; P., 88.

N.

- Neville, *Henry Allen Dugdale*. See (*Miss*) *Kate Maud Jackson*.
- Newman, *Sidney Herbert*. See *John Theodore Hewitt*.
- Norris, *Roland Victor*. See (*Miss*) *Dorothy Harrop*.

O.

- Orton, Kennedy Joseph Previté**, and **William Jacob Jones**, a crystalline bleaching powder, T., 751; P., 74.
 primary interaction of chlorine and acetanilides, T., 1456; P., 196.
 chlorination and bromination of acylanilides. A direct process; preliminary note, P., 233.
 chlorination and bromination of acylanilides. Part II. The action of the halogen acids on chloro- and bromo-acylaminobenzenes; preliminary note, P., 305.
- Orton, Kennedy Joseph Previté**. See also **William Jacob Jones**, and (*Miss*) **Alice Emily Smith**.
- Owen, (Miss) Gertrude Emily**. See **Alexander Findlay**.

P.

- Parry, (Miss) Ethel**. See **Hamilton McCombie**.
- Parry, William**, ethyl α -hydroxyisobutyrate, P., 305.
- Partington, James Riddick**. See **Arthur Lapworth**.
- Patterson, Thomas Stewart**, and **David Paterson McDonald**, the influence of solvents on the rotation of optically active compounds. Part XIV. Ethyl tartrate in benzaldehyde and in quinoline, T., 321; P., 36.
- Patterson, Thomas Stewart**, and **Harvey Hugh Montgomerie**, the influence of solvents on the rotation of optically active compounds. Part XV. Mixed solvents, T., 1128; P., 151.
- Peachey, Stanley John**. See **William Jackson Pope**.
- Perkin, Arthur George**, indoxylic acid, T., 847; P., 126.
 the colouring matters of the flowers of *Hibiscus sardariffa* and *Thespesia lampas*, T., 1855; P., 248.
 the colouring matter of cotton flowers, *Gossypium herbaceum*. Part II., T., 2181; P., 291.
 the reduction of indirubin, P., 127.
- Perkin, Arthur George**, and **Frederick Thomas**, indican. Part II., T., 793; P., 125.
- Perkin, Arthur George**. See also **T. Kametaka**, and **Frederick Thomas**.
- Perkin, Frederick Mollwo**, and **Lionel Pratt**, action of alcohols on metallic calcium, T., 159; P., 18.
- Perkin, Frederick Mollwo**. See also (*Miss*) **Mary Cunningham**.
- Perkin, William Henry, jun.**, **William Jackson Pope**, and **Otto Wallach**, optically active substances containing no asymmetric atom, 1-methylcyclohexylidene-4-acetic acid, T., 1789; P., 83, 230; discussion, P., 84.
- Perkin, William Henry, jun.**, and **Robert Robinson**, brazilin, hæmatoxylin and their derivatives. Part X. The constitution of trimethylbrazilone, of α - and β -anhydrotrimethylbrazilone, and of the corresponding hæmatoxylin derivatives, T., 381; P., 31.
- Perkin, William Henry, jun.**, **Robert Robinson**, and **Frederick Thomas**, synthesis of cotarnic acid, T., 1977; P., 262.
- Perkin, William Henry, jun.**, and **John Lionel Simonsen**, cyclobutane-1:3-dicarboxylic acid and some of its derivatives, T., 1166; P., 178.
 note on the condensation of acetone and hippuric acid, P., 164.
- Perkin, William Henry, jun.** See also **Oscar Baudisch**, (*Miss*) **Mary Elizabeth Dobson**, **Edward Hope**, and **Andrew Norman Meldrum**.
- Phillip, James Charles**, and **Frederick Basil Garner**, influence of various sodium salts on the solubility of sparingly soluble acids. Part II., T., 1466; P., 212.
- Phillips, Harry Edward William**, the electrical conductivity of phosphoric acid, T., 59.
- Pickard, Joseph Allen**. See **Gilbert Thomas Morgan**.
- Pickard, Robert Howson**, and **Joseph Kenyon**, resolution of racemic alcohols; preliminary note, P., 167.
- Pickard, Robert Howson**, and **Joseph Yates**, optically active reduced naphthoic acids. Part IV. Comparison of the rotatory powers of the di- and tetra-hydronaphthoic acids with those of phenylallylacetic, α -phenylvaleric, β -phenyl- α -ethyl-, and β -phenyl- α -methyl-propionic acids, T., 1011; P., 152.
- Pickering, Spencer Percival Umfreville**, hydration of precipitates, T., 123; P., 12.
 the carbonates of copper and the cupricarbonates, T., 1409; P., 188; discussion, P., 188.
- Pope, Frank George**, and **Hubert Howard**, the condensation of benzaldehyde with resorcinol, P., 304.
- Pope, William Jackson**, and **Stanley John Peachey**, the alkyl compounds of platinum, T., 571; P., 96.

- Pope, *William Jackson*, and *John Read*, condensation of oxymethyleneamphor with primary and secondary amino-compounds, T., 171; P., 18.
- Pope, *William Jackson*. See also *Frederic Stanley Kipping* and *William Henry Perkin, jun.*
- Power, *Frederick Belding*, and *Charles Watson Moore*, the constituents of the bark of *Prunus serotina*. Isolation of *l*-mandelonitrile glucoside, T., 243; P., 27.
the constituents of the fruit of *Ecbalium Elaterium*, T., 1985; P., 260.
- Pratt, *Lionel*. See *Frederick Mollwo Perkin*.
- Price, *Thomas Slater*, and *Lionel Manfred Jones*, the benzyl and nitrobenzyl selenosulphates and the benzyl and nitrobenzyl diselenides, T., 1729; P., 234.
- Price, *Thomas Slater*, and *Douglas Frank Twiss*, the preparation of disulphides. Part V. Diethyl esters of α -dithiodibutyric, α -dithiodiisobutyric, and α -dithiodiisovaleric acids, T., 1050; P., 165.
the preparation of disulphides. Part VI. Note on a new method of preparing disulphides, T., 1489; P., 211.
the preparation of disulphides. Part VII. The nitrobenzyl mercaptans and disulphides, T., 1725; P., 232.
the preparation of disulphides. Part III. The nitrobenzyl disulphides: a correction, P., 32.
- Prideaux, *Edmund Brydges Rudhall*, the atomic volumes of phosphorus. Part II. Phosphorus and bromine, T., 445.
- Priestley, *John Gillies*. See *Siegfried Ruhemann*.
- Pring, *John Norman*, and *William Fielding*, the preparation at high temperatures of some refractory metals from their chlorides, T., 1497; P., 215.
- Purvis, *John Edward*, the relationship between the constitution and absorption spectra of pyridine and various derivatives, T., 294; P., 14.
- Pyman, *Frank Lee*, isoquinoline derivatives. Part I. Oxidation of laudanosine, T., 1266; P., 190.
isoquinoline derivatives. Part II. The constitution of the reduction products of papaverine, T., 1610; P., 217.
isoquinoline derivatives. Part III. The oxidation of substituted 1-benzyltetrahydroisoquinolines, T., 1738; P., 230.
- Pyman, *Frank Lee*. See also *Hooper Albert Dickinson Jowett*.
- R.
- Ramsay, (*Sir*) *William*, presidential address, T., 624.
- Ramsay, (*Sir*) *William*. See also *Robert Whytlaw Gray*.
- Rây, *Prafulla Chandra*, molecular volumes of the nitrites of barium, strontium, and calcium, T., 66.
the decomposition and sublimation of ammonium nitrite, T., 345; P., 56.
- Read, *John*. See *William Jackson Pope*.
- Renouf, (*Miss*) *Nora*. See *Arthur William Crossley*.
- Reynolds, *James Emerson*, silicon researches. Part XI. Silicotetrapyrrole, T., 505.
silicon researches. Part XII. The action of silicochloroform on potassium pyrrole, T., 508.
silicon researches. Part XIII. Silicon halides and pyridine, acetonitrile, etc., T., 512.
- Rivett, *Albert Cherbury David*. See *Nevil Vincent Sidgwick*.
- Robertson, *Robert*, the velocity of decomposition of nitroglycerin by heat. Part I., T., 1241; P., 179.
- Robinson, *Fred*. See *Henry John Horstman Fenton*.
- Robinson, *Frederic William*, double and triple ferrocyanides of magnesium, aluminium, and cerium with potassium and ammonium, T., 1353; P., 195.
- Robinson, *Robert*, a new synthesis of oxazole derivatives, T., 2167; P., 295.
- Robinson, *Robert*, and *John Lionel Simonsen*, experiments on the constitution of the aloins. Part I., T., 1085; P., 153.
experiments on the constitution of the aloins; preliminary note, P., 76.
- Robinson, *Robert*. See also *William Henry Perkin, jun.*
- Ruhemann, *Siegfried*, formation of cyclohexanone derivatives from olefinic compounds, T., 109; P., 10.
action of mustard oils on the ethyl esters of malonic and cyanoacetic acids. Part II., T., 117; P., 14.
the condensation of amides with esters of acetylenic acids, T., 984; P., 87; discussion, P., 87.
diketodiphenylpyrroline and its analogues, T., 1603; P., 220.
- Ruhemann, *Siegfried*, and *John Gillies Priestley*, the action of ethyl carbamate on esters of organic acids and mustard oils, T., 449; P., 62.

Rule, Alexander. See *Alfred Theophilus de Moulipied*.

S.

Sageman, Philip John. See *John Holmes*.

Salway, Arthur Henry, the action of nitric acid on the ethers of aromatic hydroxyaldehydes, T., 1155; P., 160; discussion, P., 161.

the synthesis of substances allied to cotarnine, T., 1204; P., 175.

Salway, Arthur Henry, and *Frederic Stanley Kipping*, atmospheric oxidation of β -methylhydrindone, T., 166; P., 16.

Sand, Henry Julius Salomon, the rapid electro-analytical deposition and separation of metals. Part III. Preliminary note, P., 228.

Schneider, Wilhelm. See *Frederick George Donnan*.

Scott, Alexander, the molecular weight of tetraethylammonium bromide and the atomic weight of carbon, T., 1200; P., 173; discussion, P., 174.

the correction of weights of substances weighed in air to weights in a vacuum, P., 286.

the combustion of naphthalene and other organic substances and the atomic weight of carbon, P., 310.

Senior, Alfred, and *Arthur Compton*, the synthesis of acridines: tetramethyl-acridines, dimethylnaphthacridines, naphthaquinacridines, diquinacridines, T., 1623; P., 220.

Senior, Alfred, and *Frederick George Sheppard*, salicylidene-*m*-toluidine, a new phototropic compound; salicylideneamines: salicylamides, T., 441; P., 61.

thiotetrahydroquinazolines, methylene-carbamides, dicarbanilinomethylene-diamines and their homologues, T., 494; P., 72.

studies in phototropy and thermotropy. Part I. Arylidene- and naphthylidene-amines, T., 1943; P., 246.

Senter, George, reactivity of the halogens in organic compounds. Part III. Interaction of bromoacetic, α -bromopropionic, and α -bromobutyric acids and their sodium salts with water and with alkali, T., 1827; P., 236. viscosity and association in binary mixtures of liquids, P., 292.

Seyler, Clarence Arthur, and *Percy Vivian Lloyd*, studies of the carbonates. Part I. The equilibrium between calcium carbonate and carbonic acid, T., 1347; P., 199.

Shenstone, William Ashwell, obituary notice of, T., 2206.

Shepherd, Frederick George. See *Alfred Senior*.

Sheppard, Samuel Edward, the optical and sensitising properties of the isocyanine dyes, T., 15.

Shibata, Fūji, the action of the Grignard reagent on phthalic esters, T., 1449; P., 209.

Sidgwick, Nevil Vincent, and *Tom Sidney Moore*, the rate of reaction of the triphenylmethane dyes with acid and alkali. Part II. Brilliant-green and malachite-green, T., 889; P., 123.

Sidgwick, Nevil Vincent, and *Albert Cherbury David Rivett*, the rate of reaction of the triphenylmethane dyes with acid and alkali. Part III. Diaminotriphenylcarbinol, T., 899; P., 124.

Simonsen, John Lionel, and *Robert Storey*, syntheses with the aid of monochloromethyl ether. Part II. The action of monochloromethyl ether on the sodium derivative of ethyl acetoacetate, T., 2106; P., 290.

Simonsen, John Lionel. See also *William Henry Perkin, jun.*, and *Robert Robinson*.

Sirkar, A. Chandra, and *Jatindra M. Dutta*, the reaction between potassium permanganate and manganese sulphate in acid solution, P., 249.

Sirkar, A. Chandra. See also *Edwin Roy Watson*.

Slator, Arthur, and *Douglas Frank Twiss*, chemical dynamics of the reactions between sodium thiosulphate and organic halogen compounds. Part III., T., 93.

Smedley, (Miss) Ida, the relation between the chemical constitution and optical properties of the aromatic α - and γ -diketones, T., 218; P., 17.

note on the constitution of the carbonyl group, T., 231; P., 16.

the stereoisomeric modifications of $\alpha\beta$ -dibromobenzylacetophenone, P., 259.

Smiles, Samuel. See *Edward de Barry Barnett* and *Hans Thacher Clarke*.

Smith, (Miss) Alice Emily, and *Kennedy Joseph Previté Orton*, acids as accelerators in acetylation. Part II., T., 1060; P., 166.

Smith, Clarenc. See *Alce Duncan Mitchell*.

Smythe, John Armstrong, benzyl sulphoxide: a possible example of dynamic isomerism, T., 349.

Sonstadt, Edward, obituary notice of, T., 2209.

- Stevenson, (Sir) Thomas**, obituary notice of, T., 2213.
- Storey, Robert**. See *John Lionel Simonsen*.
- Struthers, Robert de Jersey Fleming**. See *James Ernest Marsh*.
- Sudborough, John Joseph**, and *Morton James Pryce Davis*, esterification constants of substituted acrylic acids. Part IV, T., 975; P., 147.
- Sudborough, John Joseph**, and *James Mylam Gittins*, esterification constants of substituted acrylic acids. Part III, T., 315; P., 31.
- Sudborough, John Joseph**, and *Harold Hibbert*, estimation of primary, secondary, and tertiary amines. Part I, T., 477; P., 75.
- Sudborough, John Joseph**. See also *Thomas Campbell James*.

T.

- Tasker, Hubert Sanderson**, and *Humphrey Owen Jones*, the action of mercaptans on acid chlorides. Part II. The acid chlorides of phosphorus, sulphur, and nitrogen, T., 1910; P., 247.
- Tasker, Hubert Sanderson**. See also *Humphrey Owen Jones*.
- Thole, Ferdinand Bernard**, note on the anomalous viscosity of nitrobenzene, P., 193.
- Thole, Ferdinand Bernard**. See also *Albert Ernest Dunstan* and *John Theodore Hewitt*.
- Thomas, Frederiek**, *William Popplewell Bloxam*, and *Arthur George Perkin*, indican. Part III, T., 824; P., 126.
- Thomas, Frederiek**. See also *Arthur George Perkin* and *William Henry Perkin, jun.*
- Thomas, John**, the isolation of the aromatic sulphinic acids, T., 342; P., 60.
- Thomas, William**. See *John Theodore Hewitt*.
- Thompson, Herbert Bryan**. See *Norman Leslie Gebhard*.
- Thornley, Tom**. See *Martin Onslow Forster*.
- Thorpe, Jocelyn Field**, the formation and reactions of imino-compounds. Part XI. The formation of 1-imino-2-cyanocyclopropane from adiponitrile, T., 1901; P., 243; discussion, P., 243.
- the transformation of aliphatic nitriles into alicyclic imino-compounds; preliminary note, P., 17.
- the preparation of methyl 1:1-dimethylcyclopentan-3:4-dione-2:5-dicarboxylate, P., 94.
- Thorpe, Jocelyn Field**, the nomenclature of imino-compounds and of compounds exhibiting imino-amino-isomerism, P., 309.
- Thorpe, Jocelyn Field**. See also *Stanley Robert Best*.
- Thorpe, (Sir) Thomas Edward**, note on the detection of white or ordinary phosphorus in the igniting composition of lucifer matches, T., 440; P., 73.
- note on Dr. Scott's paper on the molecular weight of tetraethylammonium bromide and the atomic weight of carbon, P., 285.
- Threlfall, Richard**, apparatus for experiments at high temperatures and pressures, and its application to the study of carbon: a correction, P., 153.
- Tinkler, Charles Kenneth**, the colour and constitution of the alkyl iodides of cyclic bases, T., 921; P., 128.
- Titherley, Arthur Walsh**, and *William Longton Hicks*, labile isomerism among the acylsalicylamide, acylhydroxyamine, and phenylbenzomethoxazine groups, T., 908; P., 95.
- Titherley, Arthur Walsh**, and (*Miss Elizabeth Worrall*), the action of phosphorus pentachloride on benzamide, T., 1143; P., 150.
- Tuck, William Bradshaw**, the constitution of hydroxyazo-compounds. Part II, T., 1809; P., 230.
- Turner, William Ernest Stephen**, a possible intramolecular change in the inactive phenylalkyloxyacetic acids; preliminary note, P., 201.
- Turner, William Ernest Stephen**. See also *Alexander Findlay*.
- Tutin, Frank**, isoamygdalin and the resolution of its hepta-acetyl derivative, T., 663; P., 118.
- Tutin, Frank, Frederic William Caton**, and *Archie Cecil Osborn Hann*, syntheses in the epinephrine series, T., 2113; P., 289.
- Tutin, Frank**, and *Hubert William Bentley Clewer*, chemical examination of eriodictyon. Part II, T., 81; P., 12.
- the constitution of chrysophanic acid and of emodin; preliminary note, P., 200.
- the constituents of *Rumex Ecklonianus*, P., 302.
- Tutin, Frank**. See also *Marmaduke Barrowcliff*.
- Twiss, Douglas Frank**. See *Thomas Slater Price* and *Arthur Slater*.

U.

Usher, Francis Lawry, the influence of non-electrolytes on the solubility of carbon dioxide in water, P., 303; discussion, P., 303.

V.

Vanstone, Ernest, the miscibility of solids, T., 590; P., 30.

Veley, Victor Herbert, the affinity values of tropine and its derivatives, T., 1. the affinity values of certain alkaloids, T., 758; P., 115; discussion, P., 116.

the rate of formation of azo-derivatives from benzenoid diamines, T., 1186; P., 175.

Vodden, Leonard. See *David Leonard Chapman*.

W.

Wade, John, and *Horace Finnemore*, ethyl ether. Part I. The influence of water and alcohol on its boiling point, T., 1842; P., 236.

Wade, John, and *Richard William Merriam*, the correction of the specific gravity of liquids for the buoyancy of air, T., 2174; P., 290.

Walker, James Wallace, and *Vernon K. Krieble*, the hydrolysis of amygdalin by acids. Part I., T., 1369; P., 203.

the amygdalins. Part I., T., 1437; P., 208.

Wallach, Otto. See *William Henry Perkin, jun.*

Walpole, George Stanley, a simple gas-drying apparatus for use with a mechanical exhaust pump, P., 97.

Walpole, George Stanley. See also *George Barger*.

Watson, Edwin Roy, the relation between the chemical constitution of monoazo-dyes and their fastness to light, P., 224.

Watson, Edwin Roy, *A. Chandra Sirkar*, and *Jatindra M. Dutta*, the relation between the chemical constitution of monoazo-dyes and their fastness to light, P., 290.

Watson, Herbert Edmeston. See *Edward Charles Cyril Baly*.

Watt, Henry Edgar, the alkaloids of *Senecio latifolius*, T., 466; P., 68.

Wechsler, Elkan. See *Arthur Lapworth*.

Wedekind, Edgar, and *Samuel Judd Lewis*, analytical investigation of zirconium metal, T., 456; P., 60.

chlorine generated by potassium permanganate; its preparation and purity, P., 59; discussion, P., 59.

Weizmann, Charles. See *(Miss) Dorothy Harrop*.

Whitby, George Stafford. See *Gilbert Thomas Morgan*.

Whiteley, (Miss) Martha Annie, and *Harold Mountain*, studies in the barbituric acid series. Part II. 1:3-Diphenyl-2-thiobarbituric acid and some coloured derivatives, P., 121.

Wilks, William Arthur Reginald. See *Henry John Horstman Fenton*.

Winmill, Thomas Field. See *John Theodore Hewitt*.

Wise, Archibald. See *Harold Hibbert*.

Wood, John Kerfoot, and *(Miss) Emma Alexander Anderson*, the constitution of the salts of barbituric acid, T., 979; P., 154.

Woodhouse, John Obins. See *William Robert Lang*.

Wootton, William Ord, amides and imides of camphoric acid; preliminary note, P., 308.

Worrall, (Miss) Elizabeth. See *Arthur Walsh Titherley*.

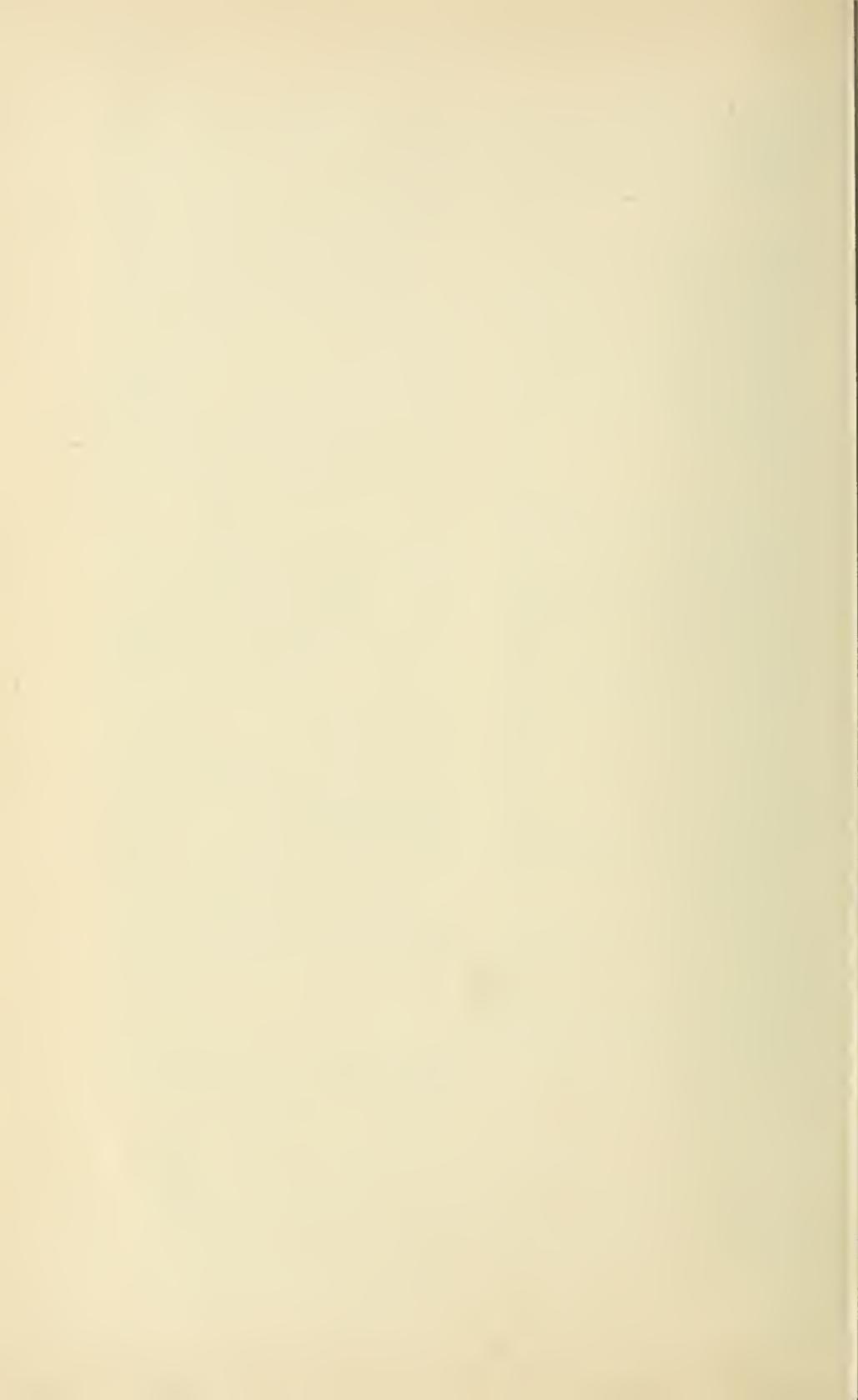
Wren, Henry, some derivatives of *l*-benzoin, T., 1583; P., 219.

racemisation phenomena observed in the study of *l*-benzoin and its derivatives, T., 1593; P., 219.

Wünsch, Donald Frederick Sandys. See *Frederick Daniel Chattaway*.

Y.

Yates, Joseph. See *Robert Howson Pickard*.



INDEX OF SUBJECTS.

TRANSACTIONS AND PROCEEDINGS. 1909.

(Marked T. and P. respectively.)

Single organic compounds of known empirical formula will be found in the Formula Index, p. 2247.

A.

- Acetanilides**, primary interaction of chlorine and (ORTON and JONES), T., 1456; P., 196.
- Acetylation**, acids as accelerators in (SMITH and ORTON), T., 1060; P., 166.
- Acid chlorides**, action of mercaptans on (JONES and TASKER), T., 1904; P., 247; (TASKER and JONES), T., 1910; P., 247.
- Acids and bases**, the relation between the strength of, and the quantitative distribution of affinity in the molecule (FLÜRSCHHEIM), T., 718; P., 22; Part II., P., 193.
- as accelerators in acetylation (SMITH and ORTON), T., 1060; P., 166.
- containing two adjacent ethenoid groups, optical activity of (HILDITCH), T., 1570; P., 214.
- influence of various sodium salts on the solubility of sparingly soluble (PHILIP and GARNER), T., 1466; P., 212.
- Acids**, aromatic, sulphinic, isolation of (THOMAS), T., 342; P., 60.
- fatty, monobasic, azoimides of (FORSTER and MÜLLER), T., 191; P., 26.
- fatty, dibasic, optical activity of (HILDITCH), T., 1578; P., 214.
- mineral, variation in the catalytic activity of, with changes in their concentration (LAPWORTH), P., 19.
- organic, action of sulphur monochloride on salts of (a convenient method of preparing anhydrides) (DENHAM), T., 1235; P., 179.
- See also Alkyloxy-acids and Hydroxy-acids.
- Acrylic acids**, substituted, esterification constants of (SUDBOROUGH and GITTINS), T., 315; P., 31; (SUDBOROUGH and DAVIS), T., 975; P., 147.
- Acyilanilides**, chlorination and bromination of (ORTON and JONES), P., 233, 305.
- Acybornylamines** (FRANKLAND and BARROW), T., 2017, 2026; P., 263.
- Adsorption** in relation to Gibbs's theory the mercury adsorbing surface (LEWIS), P., 258.
- AFFINITY, CHEMICAL:—**
- Affinity**, quantitative distribution of, in the molecule, and the relation between the strength of acids and bases (FLÜRSCHHEIM), T., 718; P., 22; Part II., P., 193.
- and electrons (FLÜRSCHHEIM), P., 261.
- of organic substances, simple method for determining the (HIEBERT), P., 57; discussion, P., 58.
- Affinity constants** of hydroxy- and alkyloxy-acids (FINDLAY, TURNER, and OWEN), T., 938; P., 146.
- Affinity values** and hydrolysis, lecture experiments to illustrate (VELEY), T., 759.
- of certain alkaloids (VELEY), T., 758; P., 115.
- of tropine and its derivatives (VELEY), T., 1.
- Dynamic isomerism**, studies of (LOWRY and DESCH), T., 807, 1340; P., 13, 192.
- benzyl sulphoxide; a possible example of (SMYTHE), T., 349.
- Chemical dynamics** of the reaction between iodine and acetone (DAWSON and LESLIE), T., 1860; P., 246.
- of the reactions between sodium thiosulphate and organic halogen compounds (SLATOR and TWISS), T., 93.
- Chemical equilibrium** between calcium carbonate and carbonic acid, and effect of dissolved salts on (SEYLER and LLOYD), T., 1347; P., 199.

AFFINITY, CHEMICAL:—

- Dissociation equilibria** in solutions, method for investigating, and its application to the study of aqueous potassium mercuri-iodide solutions (DAWSON), T., 870; P., 129.
- Hydrolysis** and affinity values, lecture experiments to illustrate (VELEY), T., 759.
- Velocity of chemical change**, determination of the, by measurement of the gases evolved (LAMPLOUGH), P., 23; discussion, P., 24.
- Velocity of formation** of azo-derivatives from benzenoid diamines (VELEY), T., 1186; P., 175.
- Velocity of hydrolysis**, influence of hydroxy- and alkyloxy-groups on the (FINDLAY and HICKMANS), T., 1004; P., 152.
- Velocity of reaction** of triphenyl-methane dyes with acid and alkali (SIDGWICK and MOORE), T., 889; P., 123; (SIDGWICK and RIVETT), T., 899; P., 124.
- Alcohols**, action of metallic calcium on (PERKIN and PRATT), T., 159; P., 18.
racemic, resolution of (PICKARD and KENYON), P., 167.
- Aldehydes and ketones**, condensation of, with the sodium derivative of ethyl cyanoacetate (HAWORTH), T., 480; P., 76; (GARDNER and HAWORTH), T., 1955; P., 250.
See also Hydroxyaldehydes.
- Aldehyde-cyanohydrins**, preparation of acyl derivatives of (FRANCIS and DAVIS), T., 1403; P., 210.
- Alkaloids**, affinity values of certain (VELEY), T., 758; P., 115.
of *Senecio latifolius* (WATT), T., 466; P., 68.
- Alkyl magnesium halides**, and tertiary amines, stability of compounds derived from (HIBBERT), P., 118.
- Alkyloxy-acids**, affinity constants of (FINDLAY, TURNER, and OWEN), T., 938; P., 146.
- Allene-carboxylic acids**, substituted, experiments on (LAPWORTH and WECHSLER), P., 307.
- Aloins**, constitution of the (ROBINSON and SIMONSEN), T., 1085; P., 76, 153.
- Aluminium** double and triple ferrocyanides with potassium and ammonium (ROBINSON), T., 1353; P., 195.
- Amides**, condensation of, with esters of acetylenic acids (RUHEMANN), T., 984; P., 87.
- Amines**, interaction of, with 2:3:5-trinitro-4-acetylamino-phenol (MELDOLA and HAY), T., 1033; P., 167.
new method for the separation of tertiary from secondary and primary (HIBBERT and WISE), P., 119.
primary, secondary, and tertiary, estimation of (SUDBOROUGH and HIBBERT), T., 477; P., 75.
tertiary, and magnesium alkyl halides, stability of compounds derived from (HIBBERT), P., 118.
- Amino-compounds**, condensation of oxy-methylenecamphor with (POPE and READ), T., 171; P., 18.
- Ammines**, metallic, configuration of (BAKER), P., 223.
- Ammonium**, double and triple ferrocyanides of magnesium, aluminium, and cerium with potassium and (ROBINSON), T., 1353; P., 195.
- Ammonium dichloroiodide** and chlorobromoiodide (CHATTAWAY), P., 163.
chromate, dichromate, and trichromate, slow decomposition of, by heat (BALL), T., 87.
perhalides (CHATTAWAY), P., 163.
nitrite, decomposition and sublimation of (RÂY), T., 345; P., 56.
- Amygdalins** (WALKER and KRIEBLE), T., 1437; P., 208.
- d*-**Amyl group**, influence of, in asymmetric synthesis (MCKENZIE and MÜLLER), T., 544; P., 88.
- Androsin**, $C_{15}H_{20}O_8$.
- Androsterol**, $C_{30}H_{50}O$.
- Anhydrides** of organic acids, preparation of (DENHAM), T., 1235; P., 179.
preparation of, by the action of thionyl chloride on salts of organic acids (DENHAM), P., 294.
- Anilides**, quantitative decomposition of (DAVIS), T., 1397; P., 197.
- Anilines**, nitro-, mechanism of reduction of (FLÜRSCHHEIM), P., 21.
- Annual General Meeting**, T., 611; P., 101.
- Antimony organic compounds** (MACKEY), T., 604; P., 98; (MORGAN, MICKLETHWAIT, and WHITBY), P., 302.
- Apocynamarin**, $C_{28}H_{36}O_6$.
Apocynum androsaemifolium, constituents of the rhizome of (MOORE), T., 734; P., 85.
- Apocynum cannabinum*, constituents of (FINNEMORE), P., 77.
- Apparatus**, gas-drying, for use with a mechanical exhaust pump (WALPOLE), P., 97.

Arsenic :—

Arsenious acid, some esters of (LANG and WOODHOUSE), P., 199.

Arsenic organic compounds (MORGAN and MICKLETHWAIT), T., 1473 ; P., 212.

Arsenic, estimation of, in organic compounds (LITTLE, CABEN, and MORGAN), T., 1477 ; P., 212.

Association and viscosity in binary mixtures of liquids (SENER), P., 292.

Asymmetric compounds, study of (KIPPING), T., 408 ; P., 55.

Atomic volumes. See Volumes.

Atomic weight of carbon (SCOTT), T., 1200 ; P., 173, 310 ; (THORPE), P., 285.

of chlorine (GRAY and BURT), T., 1633 ; P., 216.

Atomic weights, report of the International Committee on, T., 2216.

table of, T., 2219

method of harmonising the (MOIR), T., 1752 ; P., 213.

of the lighter elements, divergence of, from whole numbers (EGERTON), T., 238 ; P., 26.

Availability of hydrogen chloride in alcoholic solution, influence of water on the (LAPWORTH and PARTINGTON), P., 307.

Azine series, studies in the (HEWITT, NEWMAN, and WINMILL), T., 577 ; P., 86.

Azo-compounds, colour and constitution of (HEWITT and THOMAS), T., 1292 ; P., 190 ; (HEWITT and THOLE), T., 1393 ; P., 208.

Azo-compounds, hydroxy-, constitution of (MITCHELL and SMITH), T., 1430 ; P., 209 ; (TUCK), T., 1809 ; P., 230.

Azo-derivatives, rate of formation of, from benzenoid diamines (VELEY), T., 1186 ; P., 175.

Azo-dyes, mono-, relation between the chemical constitution and fastness to light of (WATSON), P., 224 ; (WATSON, SIRKAR, and DUTTA), P., 290.

Azoimide (*hydrazoic acid*, *hydronitric acid*) sodium salt, interaction of benzhydroximic chloride and (FORSTER), T., 184 ; P., 25.

Azoimides of monobasic aliphatic acids (FORSTER and MÜLLER), T., 191 ; P., 26.

B.

Balance Sheets of the Chemical Society and of the Research Fund. See Annual General Meeting, T., 618 ; P., 101.

Barbituric acid series, studies in the (WHITELEY and MOUNTAIN), P., 121.

Barium nitrite, molecular volume of (RÅY), T., 66.

Bases, and acids, relation between the strength of, and the quantitative distribution of affinity in the molecule (FLÜRSCHHEIM). T., 718 ; P., 22, 193.

Bismuth trioxide, solubility of, in alkali hydroxides (KNOX), T., 1760 ; P., 226.

trisulphide, solubility of, in alkali sulphides (KNOX), T., 1760 ; P., 226.

Bleaching powder, a crystalline (ORTON and JONES), T., 751 ; P., 74.

Bornylamides (FRANKLAND and BARROW), T., 2017 ; P., 263 ; T., 2026 ; P., 263.

Boron, preparation of (PRING and FIELDING), T., 1500 ; P., 215.

Bromoacetylaminobenzenes, action of halogen acids on (ORTON and JONES), P., 305.

Butter, detection of coconut oil in (CALDWELL and HURTLEY), T., 861 ; P., 73.

Butter-fat, coconut oil, and their fatty acids, distillation of (CALDWELL and HURTLEY), T., 853 ; P., 73.

C.

Cæsium, new method for the detection of (BALL), T., 2126 ; P., 284.

Calcium, action of alcohols on (PERKIN and PRATT), T., 159 ; P., 18.

Calcium carbonate and carbonic acid, equilibrium between, and effect of dissolved salts on (SEYLER and LLOYD), T., 1347 ; P., 199.

hydride, action of, on alcohols (PERKIN and PRATT), T., 161 ; P., 18.

nitrite, molecular volume of (RÅY), T., 66.

Camphane series, studies in the (FORSTER and THORNLEY), T., 942 ; P., 145 ; (FORSTER and GARLAND), T., 2051 ; P., 244.

Carbamides, chlorine derivatives of substituted (CHATTAWAY and WÜNSCH), T., 129 ; P., 11.

Carbon, atomic weight of (SCOTT), T., 1200 ; P., 173, 310 ; (THORPE), P., 285.

apparatus for experiments at high temperatures and pressures on (THRELFALL), P., 153.

Carbon dioxide, decomposition of, by the silent electric discharge (HOLT), T., 30.

- Carbon dioxide**, influence of non-electrolytes on the solubility of, in water (USHER), P., 303.
- Carbonic acid**, constitution of (FRIEND), P., 91.
and calcium carbonate, equilibrium between, and effect of dissolved salts on (SEYLER and LLOYD), T., 1347; P., 199.
- Carbonates**, estimation of, in presence of nitrites, sulphides or sulphites, by means of potassium dichromate (MARLE), T., 1491; P., 154.
studies of the (SEYLER and LLOYD), T., 1347; P., 199.
- Carboxyl group**, constitution of (SMEDLEY), T., 231; P., 16.
- Carthamine**, $C_{15}H_{11}O_7$.
- Catechol derivatives**, methylene ethers, action of phosphorus pentachloride on (EWINS), T., 1482; P., 210.
- Cerium double and triple ferrocyanides**, with potassium, sodium, and ammonium (ROBINSON), T., 1353; P., 195.
- Chemical constitution**, and absorption spectra, relation between (BALY, COLLIE, and WATSON), T., 144.
and absorption spectra of pyridine and derivatives, relation between (PURVIS), T., 294; P., 14.
and fastness to light of monoazo-dyes, relation between (WATSON), P., 224; (WATSON, SIRKAR, and DUTTA), P., 290.
and optical properties of the aromatic α - and γ -diketones (SMEDLEY), T., 218; P., 17.
and physiological action in the tropenes, relation between (JOWETT and PYMAN), T., 1020; P., 165.
and viscosity, relation between (DUNSTAN and THOLE), T., 1556; P., 219.
of the carboxyl group (SMEDLEY), T., 231; P., 16.
- Cherry bark**, wild. See *Prunus scrotina*.
- Chitin** ($C_{30}H_{50}O_{16}N_4$)_n.
- Chlorine**, atomic weight of (GRAY and BURT), T., 1633; P., 216.
and hydrogen, interaction of (CHAPMAN and MACMAHON), T., 135, 959, 1717; P., 15, 148, 224.
generated by potassium permanganate; its preparation and purity (WEDEKIND and LEWIS), P., 59; discussion, P., 59.
primary interaction of, and acetanilides (ORTON and JONES), T., 1456; P., 196.
- Chlorine**:—
- Hydrochloric acid** (*hydrogen chloride*), conductivity of, in various solvents (BALY, BURKE, and MARSDEN), T., 1103.
density and compressibility of, and adsorption of, by glass (GRAY and BURT), T., 1634; P., 216.
influence of water on the availability of, in alcoholic solution (LAPWORTH and PARTINGTON), P., 307.
- Perchlorates**, estimation of, by titanous salts (KNECHT), P., 229.
- Chloroacetylaminobenzenes**, action of halogen acids on (ORTON and JONES), P., 305.
- Chloroxylinone**, $C_{20}H_{21}O_7N$.
- Chrysoeriol**, $C_{16}H_{12}O_6$.
- Cobaltinitrites**, studies on the (CUNNINGHAM and PERKIN), T., 1562.
- Cocoon oil**, butter fat, and their fatty acids, distillation of (CALDWELL and HURTLEY), T., 853; P., 73.
- Colour** and constitution of the alkyl iodides of cyclic bases (TINKLER), T., 921; P., 128.
of azo-compounds (HEWITT and THOLE), T., 1393; P., 208; (HEWITT and THOMAS), T., 1292; P., 190.
of diazonium salts (MORGAN and ALCOCK), T., 1319; P., 202.
of aqueous solutions of violuric acid (DONNAN and SCHNEIDER), T., 956; P., 148.
- Colouring matters** of cotton flowers, *Gossypium herbaceum* (PERKIN), T., 2181; P., 291.
- Copper solutions**, ammoniacal, nature of (DAWSON), T., 370; P., 33.
- Copper carbonates** and the cupricarbonates (PICKERING), T., 1409; P., 188.
sulphate, new basic (PICKERING), T., 1417.
sodium carbonates (PICKERING), T., 1418; P., 188.
- Cupricarbonates** (PICKERING), T., 1409; P., 188.
- Cupric hydroxide**, electromotive behaviour of, in alkaline electrolytes (ALLMAND), T., 2151; P., 258.
solubility of, in ammoniacal barium, and sodium hydroxide solutions (DAWSON), T., 377; P., 33.
solubility of, in ammoniacal sulphate solutions (DAWSON), T., 370; P., 33.
- Cuprous oxide**, electromotive behaviour of, in alkaline electrolytes (ALLMAND), T., 2151; P., 258.
- Critical-solution point**, influence of, on the shape of the melting-point curve (FLASCHNER), T., 668; P., 71.

Cryoscopic experiments with two solutes present together (PATTERSON and MONTGOMERIE), T., 1138.

Crystallisation of externally compensated mixtures (KIPPING and POPE), T., 103; P., 9.

Cupric and Cuprous salts. See under Copper.

*iso***Cyanine dyes.** optical and sensitising properties of (SHEPARD), T., 15.

Cyanohydrins, condensations of (Mc-COMBIE and PARRY), T., 584; P., 95.

Cyclic bases, colour and constitution of alkyl iodides of (TINKLER), T., 921; P., 128.

Cynotoxin, $C_{20}H_{28}O_6$.

D.

Density (*specific gravity*) of liquids, correction of, for the buoyancy of air (WADE and MERRIMAN), T., 2174; P., 290.

Diamines, benzenoid, rate of formation of azo-derivatives from (VELEY), T., 1186; P., 175.

Diazoamino-compounds, constitution of (FORSTER and GARLAND), T., 2051; P., 244.

Diazohydroxylamino-compounds, and the influence of substituting groups on the stability of their molecules (GERHARD and THOMPSON), T., 767, 1115; P., 70, 149.

p-**Diazoimides**, production of, from alkyl- and aryl-sulphonyl-*p*-diamines (MORGAN and PICKARD), P., 300.

Diazonium perbromides or *N*-tribromo-substituted hydrazines, preparation and properties of (CHATTAWAY), T., 862; P., 120.

salts, colour and constitution of (MORGAN and ALCOCK), T., 1319; P., 202.

Dihydrobenzenes, substituted (CROSSLEY and RENOFF), T., 930; P., 145.

α - and γ -**Diketones**, aromatic, relation between chemical constitution and optical properties of (SMEDLEY), T., 218; P., 17.

Diphenylamine ortho-sulphoxides, intramolecular rearrangement of (BARNETT and SMILES), T., 1253; P., 74, 195.

Dissociation. See under Affinity, chemical.

Disulphides, preparation of (PRICE and TWISS), T., 1050, 1489, 1725; P., 32, 165, 211, 232.

Dynamic isomerism. See under Affinity, chemical.

E.

Ecballium Elaterium, constituents of the fruit of (POWER and MOORE), T., 1985; P., 260.

ELECTROCHEMISTRY :—

Electrons and chemical affinity (FLURSCHEIM), P., 261.

elements and (RAMSAY), T., 624; P., 108.

Elements and electrons (RAMSAY), T., 624; P., 108.

the lighter, divergence of the atomic weights of, from whole numbers (EGERTON), T., 238; P., 26.

Emulsin, hydrolysis of amygdalin by (AULD), T., 927; P., 62.

Enzymes. See Emulsin, Indimulsin.

Epinephrine series, syntheses in the (TUTIN, CATON, and HANN), T., 2113; P., 289.

Equilibrium of sodium sulphite with water (HARTLEY and BARRETT), T., 1178; P., 164.

Equilibrium, chemical. See under Affinity, chemical.

Ergot, isolation and synthesis of *p*-hydroxyphenylethylamine, an active principle of (BARGER), T., 1123; P., 162.

Eriodictyon, chemical examination of (TUTIN and CLEWER), T., 81; P., 12.

Eriodonol, $C_{19}H_{18}O_7$.

Esterification constants of substituted acrylic acids (SUDBOROUGH and GITTINGS), T., 315; P., 31; (SUDBOROUGH and DAVIS), T., 975; P., 147.

Esters of organic acids, action of ethyl carbamate on (RUHEMANN and PRIESTLEY), T., 449; P., 62.

Ethenoid groups, optical activity of acids containing two adjacent (HILDITCH), T., 1570; P., 214.

F.

Ferric compounds. See under Iron.

Ferrocyanides. See Iron organic compounds.

G.

Gases, ignition-temperatures of (DIXON and COWARD), T., 514; P., 67.

Glasses, formation of (COBB), P., 165.

Glazes, formation of (COBB), P., 165.

Glucose derivatives, constitution of (IRVINE and GILMOUR), T., 1545; P., 218.

Glucosides. See Androsin, Gossypitrin, Quercimeritrin, *iso*Quercitrin.

Glycide aryl ethers, action of ammonia on (BOYD and KNOWLTON), T., 1802; P., 235.

Gossypetin, $C_{15}H_{16}O_8$.
Gossypitrin, $C_{21}H_{20}O_{13}$.
Grignard reagent, action of, on phthalic esters (SHIBATA), T., 1449; P., 209.

H.

Halogen compounds, organic, the chemical dynamics of the reactions between sodium thiosulphate and (SLATOR and TWISS), T., 93.
Halogens, action of, on aromatic hydrazines (CHATTAWAY), T., 1065; P., 147.
 reactivity of the, in organic compounds (SENDER), T., 1827; P., 236.
Hantzsch-Werner hypothesis, an interpretation of the (FORSTER and DUNN), T., 425; P., 68.
Hemp, Canadian. See *Apocynum cannabinum*.
Heterocyclic compounds, formation of (LE SUEUR), T., 273; P., 36.
*cyclo***Hexanone derivatives**, formation of, from olefinic compounds (RUHEMANN), T., 109; P., 10.
Hibiscetin, from *Hibiscus sabdariffa*, and its acetyl derivative (PERKIN), T., 1858; P., 248.
Hibiscus sabdariffa, colouring matters of flowers of (PERKIN), T., 1855; P., 248.
Homoandrosterol, $C_{27}H_{44}O$.
Hydration of precipitates (PICKERING), T., 123; P., 12.
 in solution and viscosity (DUNSTAN and THOLE), T., 1556; P., 219.
Hydrazine sulphate, preparation of, from *p*-urazine (CHATTAWAY), T., 237; P., 11.
Hydrazines, aromatic, action of halogens on (CHATTAWAY), T., 1065; P., 147.
N-tribromo-substituted (diazonium *per*bromides), preparation and properties of (CHATTAWAY), T., 862; P., 120.
Hydroacridines, formation of (POPE and HOWARD), P., 304.
Hydrochloric acid. See under Chlorine.
Hydrogen and chlorine, interaction of (CHAPMAN and MACMAHON), T., 135, 959, 1717; P., 15, 148, 224.
Hydrogen chloride. See under Chlorine.
peroxide, production of ozone in the interaction between sulphur dioxide and (FERRABOSCHI), P., 179.
Hydrolysis. See under Affinity, chemical.
Hydroxy-acids, affinity constants of (FINDLAY, TURNER, and OWEN), T., 938; P., 146.

Hydroxyaldehydes, action of nitric acid on the ethers of aromatic (SALWAY), T., 1155; P., 160.
Hydroxyl derivatives, estimation of, in mixtures of organic compounds (HIBBERT), P., 57.

I.

Ignition temperature. See under Thermochemistry.
Imino-compounds, alicyclic, transformation of aliphatic nitriles into (THORPE), P., 17.
 formation and reactions of (BEST and THORPE), T., 8, 261, 685, 1506; P., 28, 92, 216; (THORPE), T., 1901; P., 244.
 nomenclature of (THORPE), P., 309.
Indimulsin, the enzyme of indician, and solubility of (THOMAS, BLOXAM, and PERKIN), T., 824; P., 126.
Iodides. See under Iodine and Polyiodides.
Iodine and acetone, dynamics of the reaction between (DAWSON and LESLIE), T., 1860; P., 246.
Iodine dioxide, properties and reactions of (MUIR), T., 656; P., 88.
Iodides, alkyl, of cyclic bases, colour and constitution of (TINKLER), T., 921; P., 128.
Iron, action of steam on (FRIEND), P., 90.
 rusting of (MOOLY), P., 34.
Ferric salts of aromatic sulphinic acids, reactions of (THOMAS), T., 343.
Iron organic compounds:—
Ferrocyanides, double and triple, of magnesium, aluminium, and cerium with potassium and ammonium (ROBINSON), T., 1353; P., 195.
Iron, estimation of, by permanganate in the presence of hydrogen chloride (FRIEND), T., 1228; P., 150.
 ferrous, estimation of small quantities of, by potassium permanganate in the presence of hydrogen chloride (FRIEND), P., 224.
Isomeric change and absorption spectra, relation between (LOWRY and DESCH), T., 807, 1340; P., 13, 192.
Isomerism, dynamic. See under Affinity, chemical.
 labile, among the acylsalicylamide, acylhydroxyamine and phenylbenzometoxazine groups (TITHERLEY and HICKS), T., 908; P., 95.

K.

Ketimine-enamic isomerism (THORPE), P., 309.

Ketones and aldehydes, condensation of, with the sodium derivative of ethyl cyanoacetate (HAWORTH), T., 480; P., 76; (GARDNER and HAWORTH), T., 1955; P., 250.

Ketones, hydroaromatic (CROSSLEY and GILLING), T., 19.

L.

Lead cobaltinitrite (CUNNINGHAM and PERKIN), T., 1569.

sulphate, solubility of, in concentrated solutions of sodium and potassium acetates (FOX), T., 878; P., 128.

Liquids, correction of the specific gravity of, for the buoyancy of air (WADE and MERRIMAN), T., 2174; P., 290. volume and temperature changes attending mixture of (PATTERSON and MONTGOMERIE), T., 1136.

Lithium nitrate, electrical conductivity and absorption spectra of, in various solvents (BALY, BURKE, and MARSDEN), T., 1101; P., 144.

M.

Magnesium double and triple ferrocyanides with potassium and ammonium (ROBINSON), T., 1353; P., 195.

Magnesium organic compounds:—

Magnesium alkyl halides and tertiary amines, stability of compounds derived from (HIBBERT), P., 118.

Manganese sulphate and potassium permanganate, reaction between, in acid solution (SIRKAR and DUTTA), P., 249.

Matches, lucifer, detection of white phosphorus in the igniting composition of (THORPE), T., 440; P., 73.

Melting-point curve, influence of a critical-solution point on the shape of the (FLASCHNER), T., 668; P., 71.

Melting-point curves of mixtures of *o*- and *p*-chloroacetanilides (JONES and ORTON), T., 1059.

Memorial lectures, Gibbs (CLARKE), T., 1299; Mendel'eff (TILDEN), T., 2077.

Mercaptans, action of, on acid chlorides (JONES and TASKER), T., 1904; P., 247; (TASKER and JONES), T., 1910; P., 247.

Mercury, volumetric estimation of (KNOX), T., 1768; P., 227.

Metals, rapid electro-analytical deposition and separation of (SAND), P., 228.

refractory, preparation at high temperatures of, from their chlorides (PRING and FIELDING), T., 1497; P., 215.

Molecular complexity in the liquid state (HOLMES and SAGEMAN), T., 1928.

Molecular volumes. See Volumes molecular.

Molybdenum, preparation of (PRING and FIELDING), T., 1504; P., 215.

Morphotropic relationships between the derivatives of picric acid (JERUSALEM), T., 1275; P., 201.

Mustard oils, action of, on the ethyl esters of malonic and cyanoacetic acids (RUHEMANN), T., 117; P., 14.

action of ethyl carbamate on (RUHEMANN and PRIESTLEY), T., 449; P., 62.

N.

Naphthoic acids, optically active reduced (PICKARD and YATES), T., 1011; P., 152.

Nitrates. See under Nitrogen.

Nitriles, aliphatic, transformation of, into alicyclic imino-compounds (THORPE), P., 17.

Nitrites. See under Nitrogen.

Nitrogen chloride (CHAPMAN and VODDEN), T., 133; P., 15.

Nitrates, absorption spectra of, in relation to the ionic theory (BALY, BURKE, and MARSDEN), T., 1096; P., 144.

Nitrites, action of carbon dioxide on (MARLE), P., 74.

Nitrosyl chloride, action of mercaptans on (TASKER and JONES), T., 1910; P., 247.

O.

Obituary notices:—

Bennett Hooper Brough, T., 2202.

Richard John Friswell, T., 2204.

William Ashwell Shenstone, T., 2206.

Edward Sonstadt, T., 2209.

Sir Thomas Stevenson, T., 2213.

Olefinic compounds, formation of cyclohexanone derivatives from (RUHEMANN), T., 109; P., 10.

Optical activity, properties, and Optically active compounds. See under Photochemistry.

Organic compounds, reactivity of the halogens in (SESTER), T., 1827; P., 236.

Oxazole derivatives, new synthesis of (ROBINSON), T., 2167; P., 295.

Oxidation, atmospheric, of β -methylhydrindone (SALWAY and KIPPING), T., 166; P., 16.

Oximino-group, configuration of the (MILLS and BAIN), P., 177.

Oxydases (GORTNER), P., 306.

- Oxygen**, compressibility of (GRAY and BIRT), T., 1657; P., 216.
retarding effect of, on rate of interaction of chlorine and hydrogen (CHAPMAN and MACMAHON), T., 959; P., 148.
- Ozone**, production of, in the interaction between hydrogen dioxide and sulphur dioxide (FERRABOSCHI), P., 179.

P.

- Perchlorates**. See under Chlorine.
- Phenol derivatives** containing a mobile nitro-group, syntheses with (MELDOLA and HAY), T., 1033; P., 167.
- Phenols**, iodination of (GARDNER and HODGSON), T., 1819.
- Phenols**, nitro-, mechanism of reduction of (FLÜRSCHHEIM), P., 21.
- Phenylalkoxyacetic acids**, possible intramolecular change in the inactive (TURNER), P., 201.
- Phosphorus**, atomic volumes of (PRIDEAUX), T., 445.
white or ordinary, detection of, in igniting composition of lucifer matches (THORPE), T., 440; P., 73.
- Phosphorus pentabromide**, expansion of (PRIDEAUX), T., 445.
- Phosphoric acid**, alkaloidal phenyl *p*-tolyl esters of (LUFF and KIPPING), T., 2002.
electrical conductivity of (PHILLIPS), T., 59.
isomeric derivatives of (KIPPING and LUFF), P., 203.
resolution of asymmetrical derivatives of (LUFF and KIPPING), T., 1993; P., 256.

PHOTOCHEMISTRY:—

- Photosensitive solutions**, action of β -rays on (FLASCHNER), T., 327; P., 34.
- Optical activity**, effect of contiguous unsaturated groups on (HILDITCH), T., 331, 1570, 1578; P., 29, 214.
- Optically active compounds**, effect of solvents on the rotation of (PATERSON and McDONALD), T., 321; P., 36; (PATERSON and MONTGOMERIE), T., 1128; P., 151.
- Optically active substances** containing no asymmetric atom (PERKIN, POPE, and WALLACH), T., 1789; P., 230.
- Optical properties of α - and γ -diketones** and chemical constitution, relation between (SMEDLEY), T., 218; P., 17.

PHOTOCHEMISTRY:—

- β -Rays**, action of, on photosensitive solutions (FLASCHNER), T., 327; P., 34.
- Refractive power** and chemical activity of sulphur compounds, relation between (CLARKE and SMILES), T., 992; P., 145.
- Rotation of optically active compounds**, effect of solvents on (PATERSON and McDONALD), T., 321; P., 36; (PATERSON and MONTGOMERIE), T., 1128; P., 151.
- Spectra**, absorption, and chemical constitution, relation between (BALY, COLLIE, and WATSON), T., 144.
and constitution of pyridine and derivatives, relation between (PURVIS), T., 294; P., 14.
and isomeric change, relationship between (LOWRY and DESCH), T., 807, 1340; P., 13, 192.
of hydroxyazo - compounds and quinonehydrazones (TUCK), T., 1809; P., 230.
of the nitrates in relation to the ionic theory, and influence of carbon dioxide on (BALY, BURKE, and MARSDEN), T., 1096; P., 144.
of sulphonic derivatives of camphor (LOWRY and DESCH), T., 1340; P., 192.
- Photosensitive solutions**. See under Photochemistry.
- Phototropic compound**, a new (SENIER and SHEPHEARD), T., 441; P., 61.
- Phototropy** and thermotropy, studies in (SENIER and SHEPHEARD), T., 1943; P., 246.
- Phthalic esters**, action of the Grignard reagent on (SHIBATA), T., 1449; P., 209.
- Phycocerythrin**, the pigment of the red alga (HANSON), P., 117; discussion, P., 117.
- Physiological action** and chemical constitution in the tropeines, relation between (JOWETT and PYMAN), T., 1020; P., 165.
- Picrates**, crystallography of (JERUSALEM), T., 1278.
- Platinum organic compounds** (POPE and PEACHEY), T., 571; P., 96.
- Potassium double and triple ferrocyanides** with magnesium, aluminum, and cerium and ammonium (ROBINSON), T., 1353; P., 195.
- Potassium acetate-potassium sulphate**, the system, at 25° (FOX), T., 885; P., 128.

- Potassium dichromate**, action of, on carbonates, nitrites and mixtures of carbonates and nitrites, carbonates and sulphites, and carbonates and sulphides (MARLE, T., 1492; P., 154.
- cobaltinitrite, composition of (CUNNINGHAM and PERKIN), T., 1567.
- permanganate and manganese sulphate, reaction between, in acid solution (SIRKAR and DUTTA), P., 249.
- mercuri-iodide solutions, study of (DAWSON, T., 870; P., 129.
- mercuri-iodide containing camphor of crystallisation (MARSH and STRUTHERS), T., 1788.
- Polynitrophenols**, constitution of, in alkaline solution (BUTLE and HEWITT), T., 1755; P., 231.
- Precipitates**, hydration of (PICKERING), T., 123; P., 12.
- Prunus scrotina*, constituents of bark of (POWER and MOORE), T., 243; P., 27.
- Pyridine compounds**, relation between constitution and absorption spectra of (PURVIS), T., 294; P., 14.
- Pyridine bases**, miscibility of, with water, and influence of a critical-solution point on the shape of the melting-point curve (FLASCHNER), T., 668; P., 71.
- Pyrones** and allied compounds, relation between absorption spectra and chemical constitution of (BALY, COLLIE, and WATSON), T., 144.

Q.

- Quercimeritrin**, $C_{21}H_{20}O_{12}$.
- iso*Quercitrin, $C_{21}H_{20}O_{12}$.
- iso*Quinoline derivatives (PYMAN), T., 1266, 1738; P., 190, 230.

R.

- Racemisation** phenomena observed in the study of *l*-benzoin and its derivatives (WREN), T., 1593; P., 219.
- Radium**, table of products from emanation, liquid and solid (GRAY and RAMSAY), P., 82.
- some physical properties of (GRAY and RAMSAY), T., 1073; P., 161.
- Rays**. See under Photochemistry.
- Refractive power**. See under Photochemistry.
- Rotation**. See under Photochemistry.
- Rubidium**, new method for the detection of (BALL), T., 2126; P., 284.

- Rumex ecklonianus*, constituents of (TUTIN and CLEWER), P., 302.

S.

- Saponification**. See Hydrolysis under Affinity, chemical.
- Satinwood**, East Indian (*Chloroxylon swietenia*), chloroxylonine from (AVLD), T., 964; P., 148.
- Senecifolic acid**, $C_{10}H_{16}O_6$.
- Senecifolidine**, $C_{18}H_{25}O_7N$.
- Senecifoline**, $C_{18}H_{27}O_8N$.
- Senecifolinine**, $C_8H_{11}O_2N$.
- Senecio latifolius*, alkaloids of (WATT), T., 466; P., 68.
- Silicates**, formation of (COBB), P., 165.
- Silicochloroform**, action of, on potassium pyrrole (REYNOLDS), T., 508.
- Silicon**, preparation of (PRING and FIELDING), T., 1501; P., 215.
- halides and pyridine, acetonitrile, etc. (REYNOLDS), T., 512.
- Silicon tetrabromide**, additive compounds of, with pyridine, acetonitrile, and propionitrile (REYNOLDS), T., 513.
- tetrachloride, benzyl and ethyl derivatives of (MARTIN and KIPPING), T., 302; P., 27.
- Silicon organic compounds** (KIPPING and DAVIS), T., 69; P., 9; (REYNOLDS), T., 505, 508, 512.
- Silver**, estimation of, in presence of mercury (KNOX), T., 1768; P., 227.
- Silver cobaltinitrite** (CUNNINGHAM and PERKIN), T., 1568.
- Sodium**, new method for the detection of (BALL), T., 2126; P., 284.
- Sodium acetate-sodium sulphate** decahydrate, the system, at 25° (FOX), T., 888; P., 128.
- carbonate, spontaneous crystallisation of solutions of (JONES), T., 1672; P., 213.
- cobaltinitrite, preparation and composition of (CUNNINGHAM and PERKIN), T., 1568.
- sulphite and its equilibrium with water (HARTLEY and BARRETT), T., 1178; P., 164.
- thiosulphate, chemical dynamics of the reactions between, and organic halogen compounds (SLATOR and TWISS), T., 93.
- spontaneous crystallisation of solutions of (JONES), T., 1672; P., 213.
- cerium ferrocyanide (ROBINSON), T., 1359.
- copper carbonates (PICKERING), T., 1418; P., 188.

- Solid solutions.** See Solutions, solid.
- Solids**, the miscibility of (*solid solutions*) (VANSTONE), T., 590; P., 30.
- Solubility** of sparingly soluble acids, influence of various sodium salts on (PHILIP and GARNER), T., 1466; P., 212.
- Solution**, hydration in, and viscosity (DUNSTAN and THOLE), T., 1556; P., 219.
- Solutions**, contributions to the theory of (HOLMES and SAGEMAN), T., 1919; P., 231.
method for investigating dissociation equilibria in, and its application to the study of aqueous potassium mercuri-iodide solutions (DAWSON), T., 870; P., 129.
solid, of camphor and borneol, benzil and benzoin, and menthone and menthol, physical properties of (VANSTONE), T., 590; P., 30.
- Solvents**, influence of, on the rotation of optically active compounds (PATTERSON and McDONALD), T., 321; P., 36; (PATTERSON and MONTGOMERIE), T., 1128; P., 151.
- Spectra.** See under Photochemistry.
- Steric hindrance**, experiments with secondary amines with reference to (MELDOLA and HAY), T., 1037; P., 167.
- Steric influence**, a study in (DAVIS), T., 1397; P., 197.
- Strontium nitrite**, molecular volume of (RAY), T., 66.
- Styphnates**, crystallography of (JERUSALEM), T., 1278.
- Substance**, $I_2O_4 \cdot 3SO_3$, from iodine dioxide and sulphur trioxide (MUIR), T., 660; P., 89.
 $I_2O_5 \cdot 2SO_3$, from iodine pentoxide and sulphur trioxide (MUIR), T., 662; P., 89.
- Sulphates.** See under Sulphur.
- Sulthinic acids**, aromatic, isolation of (THOMAS), T., 342; P., 60.
- Sulphur** :—
Thionyl chloride, action of mercaptans on (TASKER and JONES), T., 1910; P., 247.
Sulphuryl chloride, action of mercaptans on (TASKER and JONES), T., 1910; P., 247.
Sulphur monochloride, action of, on salts of organic acids (DENHAM), T., 1235; P., 179.
dioxide, production of ozone in the interaction between hydrogen peroxide and (FERRABOSCHI), P., 179.
Sulphuric acid, constitution of (FRIEND), P., 91.
- Sulphur** :—
Sulphurous acid, constitution of (FRIEND), P., 91.
Sulphates, volumetric estimation of (MITCHELL and SMITH), T., 2198; P., 291.
Sulphur organic compounds, relation between refractive power and chemical activity of (CLARKE and SMILES), T., 992; P., 145.
Synthesis, asymmetric, studies in (McKENZIE and MÜLLER), T., 544; P., 83; (McKENZIE and HUMPHRIES), T., 1105; P., 164.
- T.**
- Temperature.** See under Thermochemistry.
- Tephrosia purpurea*, a glucoside from (CLARKE and BANERJEE), P., 16.
- Terpenes**, chemistry of (HENDERSON and AGNEW), T., 289; P., 35; (HENDERSON and CAMERON), T., 969; P., 151.
- Thallium cobaltinitrite** (CUNNINGHAM and PERKIN), T., 1569.
- THERMOCHEMISTRY** :—
Heat of mixture of various liquids (PATTERSON and MONTGOMERIE), T., 1136.
Temperatures, high, and high pressures, apparatus for experiments at (THRELFALL), P., 153.
Ignition temperature of gases (DIXON and COWARD), T., 514; P., 67.
Thermotropy and phototropy, studies in (SENER and SHEPHEARD), T., 1943; P., 246.
Thespsia lampas, colouring matters of flowers of (PERKIN), T., 1855; P., 248.
Thiocarbamides, action of hydrogen dioxide on (BARNETT), P., 305.
Triazo-group, the (FORSTER), T., 184, 433; P., 25, 69; (FORSTER and MÜLLER), T., 191, 2072; P., 26, 291.
Triphenylmethane dyes, rate of reaction of, with acid and alkali (SIDGWICK and MOORE), T., 889; P., 123; (SIDGWICK and RIVETT), T., 899; P., 124.
Tropeines, relation between chemical constitution and physiological action in the (JOWETT and PYMAN), T., 1020; P., 165.
Tungsten, preparation of (PRING and FIELDING), T., 1502; P., 215.
volumetric estimation of (KNECHT and HIBBERT), P., 227.
Tyrosinase, new variety of (GORTNER), P., 306.

U.

Unsaturated compounds, theory regarding the configuration of certain (BAKER), P., 223.

Unsaturated groups, contiguous, effect of, on optical activity (HILDITCH), T., 331, 1570, 1578 ; P., 29, 214.

V.

Vanadium, colorimetric estimation of small quantities of (GREGORY), P., 232.

Vapour pressures, measurement of (CUMMING), T., 1772 ; P., 237.

Velocity of hydrolysis. See under Affinity, chemical.

Violuric acid, thio-, group, coloured salts and derivatives of the (ISHERWOOD), P., 120.

Viscosity and association in binary mixtures of liquids (SENER), P., 292.

and chemical constitution, relation between (DUNSTAN and THOLE), T., 1556 ; P., 219.

and hydration in solution (DUNSTAN and THOLE), T., 1556 ; P., 219.

Volumes, atomic, of phosphorus (PRIDEAUX), T., 445.

molecular, of the nitrites of barium, strontium, and calcium (RAY), T., 66.

W.

Walden inversion, experiments on the (MCKENZIE and CLOUGH), T., 777 ; P., 70.

Water, constitution of (PICKERING), T., 127.

Weights, correction of, of substances weighed in air to weights in a vacuum (SCOTT), P., 286.

Woods, irritant, examination of (AULD), T., 964 ; P., 148.

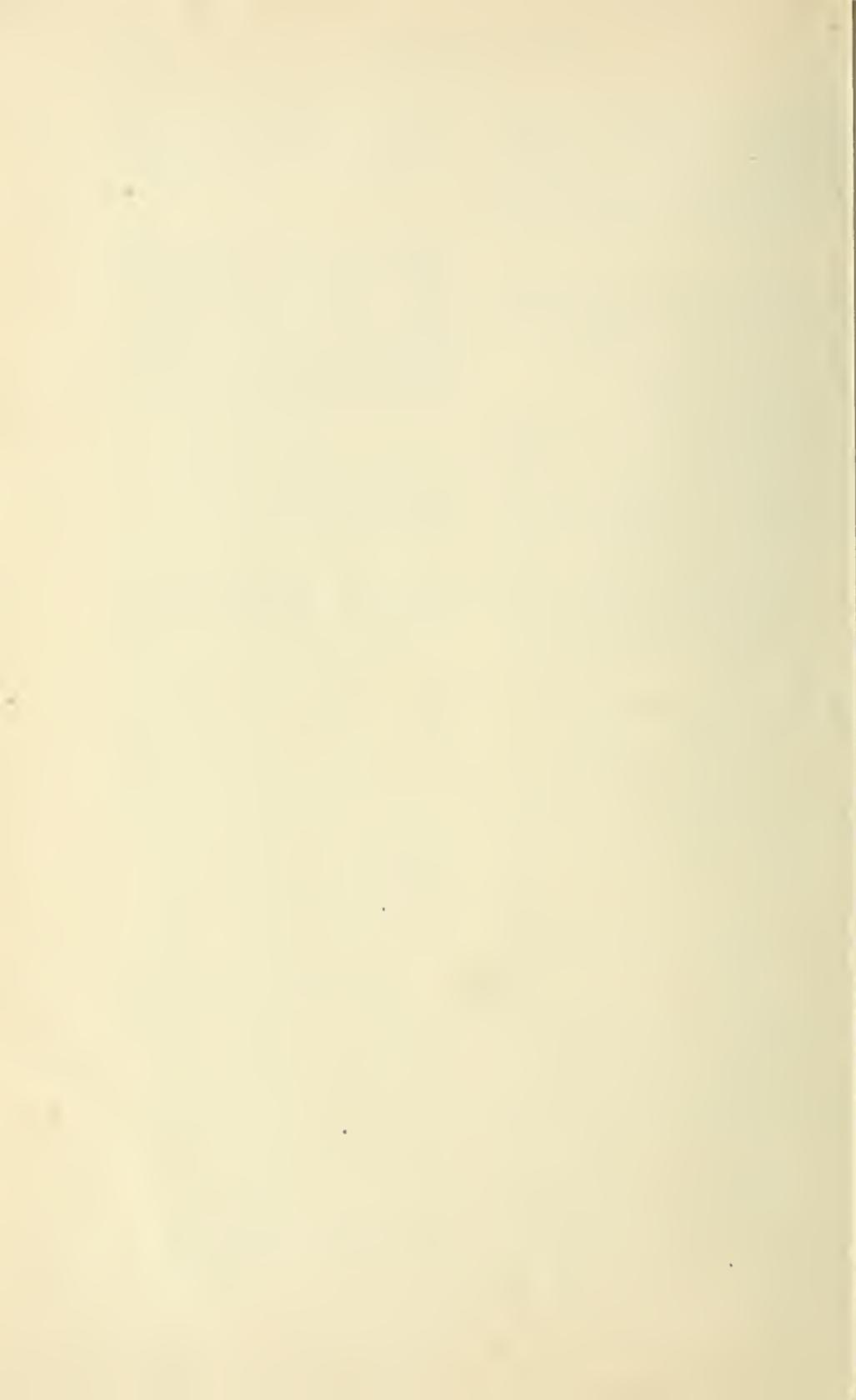
X.

Xanthenes, formation of (POPE and HOWARD), P., 304.

Xanthoeridol, $C_{18}H_{14}O_7$.

Z.

Zirconium metal, analytical investigation of (WEDEKIND and LEWIS), T., 456 ; P., 60.



FORMULA INDEX.

THE following index of organic compounds of known empirical formula is arranged according to Richter's system (see *Lexikon der Kohlenstoff-Verbindungen*).

The elements are given in the order C, H, O, N, Cl, Br, I, F, S, P, and the remainder alphabetically.

The compounds are arranged—

Firstly, in groups according to the number of carbon atoms (thus C₁ group, C₂ group, etc.).

Secondly, according to the number of other elements besides carbon contained in the molecule (thus 5 IV indicates that the molecule contains five carbon atoms and four other elements).

Thirdly, according to the nature of the elements present in the molecule (given in the above order).

Fourthly, according to the number of atoms of each single element (except carbon) present in the molecule.

Simple metallic salts of acids are indexed under the respective acids.

Simple salts of bases (for example, hydrochlorides, platinichlorides, and picrates), when described for the purpose of further identifying the base, are indexed under the latter.

C₁ Group.

- CH₂O₂ Formic acid, constitution of (FRIEND), P., 91.
CH₄O Methyl alcohol, viscosity-concentration curves for, and water (DUNSTAN and THOLE), T., 1559; P., 219.
CH₅N Methylamine, preparation and crystallography of the styphnate (JERUSALEM), T., 1285; cobaltinitrite of (CUNNINGHAM and PERKIN), T., 1564.

1 III

- CH₄ON₂ Carbamide, synthesis of *p*-urazine from (CHATTAWAY), T., 235; P., 10.

1 IV

- CH₂ON₂Cl₂ Dichlorocarbamide, preparation of (CHATTAWAY), T., 464; P., 72.

C₂ Group.

- C₂H₄O₂ Acetic acid, action of sulphur monochloride on silver salt of (DENHAM), T., 1238; P., 179; viscosity-concentration curves for, and water (DUNSTAN and THOLE), T., 1559; P., 219.
C₂H₄Br₂ Ethylene dibromide, action of, on methylaniline (DUNLOP and JONES), T., 416; P., 61.
C₂H₆O Ethyl alcohol, viscosity-concentration curves for, and water (DUNSTAN and THOLE), T., 1559; P., 219.
C₂H₇N Dimethylamine, preparation and crystallography of the styphnate of (JERUSALEM), T., 1285.
Ethylamine, preparation of cobaltinitrite of (CUNNINGHAM and PERKIN), T., 1565; preparation and crystallography of the styphnate of (JERUSALEM), T., 1287; condensation of dimethyldihydroresorcin with (HAAS), T., 421; P., 19.
C₂O₂Cl₂ Oxalyl chloride, action of mercaptans on (JONES and TASKER), T., 1904; P., 247.

2 III

- $C_2H_2O_3S_2$ Dithio-oxalic acid, ammonium, potassium, and potassium nickelosalts (JONES and TASKER), T., 1906; P., 160, 247.
 $C_2H_2O_3S$ Thio-oxalic acid, potassium salt (JONES and TASKER), P., 160.
 $C_2H_3O_2Br$ Bromoacetic acid, interaction of, and its sodium salt, with water and with alkali (SENDER), T., 1827; P., 236.
 $C_2H_4O_2N_4$ *p*-Urazine, synthesis from carbamide (CHATTAWAY), T., 235; P., 10.
 C_2H_5OCl Monochloromethyl ether, syntheses with the aid of (SIMONSEN and STOREY), T., 2106; P., 290.

2 IV

- $C_2H_5ON_2Cl$ Triazoacetyl chloride (FORSTER and MÜLLER), T., 200.
 $C_2H_3ON_2Cl_2$ Methyltrichlorocarbamide (CHATTAWAY and WÜNSCH), T., 131.

C₃ Group.

- C_3H_6O Acetone, dynamics of the reaction between iodine and (DAWSON and LESLIE), T., 1860; P., 246; condensation of, with hippuric acid (PERKIN and SIMONSEN), P., 164.
 $C_3H_6O_2$ Propionic acid, action of sulphur monochloride on silver salt of (DENHAM), T., 1238.
 $C_3H_6O_2$ *d*-Lactic acid, asymmetric synthesis of (McKENZIE and MÜLLER), T., 545.
 C_3H_7O *n*-Propyl alcohol, viscosity-concentration curves for, and water (DUNSTAN and THOLE), T., 1559; P., 219.
 C_3H_9N Trimethylamine, preparation and crystallography of the styphnate of (JERUSALEM), T., 1286.

3 III

- $C_3H_4ON_2$ *iso*Iminazolone (FENTON and WILKS), T., 1329; P., 192.
 C_3H_5OCl Epichlorohydrin, action of potassium hydroxide on, in presence of monohydric phenols (BOYD and MARLE), T., 1807; P., 235.
 $C_3H_5O_2Br$ α -Bromopropionic acid, interaction of, and its sodium salt, with water and with alkali (SENDER), T., 1827; P., 236.
 $C_3H_5O_9N_3$ Glyceryl trinitrate (nitroglycerin), velocity of decomposition of, by heat (ROBERTSON), T., 1241; P., 179.
 $C_3H_7O_2N$ Ethyl carbamate, action of, on esters of organic acids and thiocarbimides (RUHEMANN and PRIESTLEY), T., 449; P., 62.
 $C_3H_5O_3Sb$ Methyl antimonite (MACKEY), T., 607; P., 98.
 C_3H_9ClPt Trimethylplatinic chloride (POPE and PEACHEY), T., 575.
 C_3H_9IPT Trimethylplatinic iodide (POPE and PEACHEY), T., 571.
 $C_3H_{10}OPt$ Trimethylplatinic hydroxide (POPE and PEACHEY), T., 573.

3 IV

- $C_3H_5ON_2Cl_3$ Ethyltrichlorocarbamide (CHATTAWAY and WÜNSCH), T., 133.
 $C_3H_5O_2N_2Cl$ Acetylchlorocarbamide (CHATTAWAY and WÜNSCH), T., 129.
 $C_3H_6ON_2Cl_2$ Ethyldichlorocarbamide (CHATTAWAY and WÜNSCH), T., 132.
 s-Dimethyldichlorocarbamide (CHATTAWAY and WÜNSCH), T., 131.
 as-Dimethyldichlorocarbamide (CHATTAWAY and WÜNSCH), T., 132.
 $C_3H_{12}N_2IPT$ Diamminotrimethylplatinic iodide (POPE and PEACHEY), T., 573.
 $C_3H_{16}O_4N_2Cl_2$ 8:9-Dichloro-7:10-dianilino-1:6-dihydroxynaphthacenequinone (HARROP, NORRIS, and WEIZMANN), T., 288.

C₄ Group.

- C₄H₅N Pyrrole, preparation of, and action of silicochloroform on the potassium derivative of (REYNOLDS), T., 508.
- C₄H₆O₃ *d*-α-Methylglycidic acid, potassium salt (KAY), T., 563; P., 90.
- C₄H₆O₆ Tartaric acid, substituted amides of (JACKSON and NEVILLE), P., 226; resolution of the *dl*-acid (KIPPING), T., 412; P., 56.
- C₄H₈O₄ *d*-α-Methylglyceric acid, conversion of *d*-β-amino-α-hydroxyisobutyric acid into, and potassium salt of (KAY), T., 560; P., 90.
- C₄H₁₀O Ethyl ether, influence of water and alcohol on the boiling point of (WADE and FINNEMORE), T., 1842; P., 236.
- C₄H₁₁N Diethylamine, cobaltinitrite of (CUNNINGHAM and PERKIN), T., 1565

4 III

- C₄H₈O₄N₂ Tetraketopiperazine, reactions of (DE MOULPIED and RULE), T., 549; P., 71.
- C₄H₃O₄N₃ Violuric acid, colour of aqueous solutions of (DONNAN and SCHNEIDER), T., 956; P., 148.
- C₄H₄O₃N₂ Barbituric acid, constitution of the salts of (WOOD and ANDERSON), T., 979; P., 154.
- C₄H₄O₃N₆ Triazoacetic anhydride (FORSTER and MÜLLER), T., 201.
- C₄H₆O₃N₆ Triazoethyl triazoacetate (FORSTER and MÜLLER), T., 200.
- C₄H₆O₂S₂ Methyl dithio-oxalate (JONES and TASKER), T., 1906; P., 247.
- C₄H₆O₄S₂ Substance, from action of sulphur monochloride on silver acetate (DENHAM), T., 1238.
- C₄H₇O₂N₃ *l*-α-Triazobutyric acid (FORSTER and MÜLLER), T., 195.
- C₄H₇O₂Br α-Bromobutyric acid, interaction of, and its sodium salt, with water and with alkali (SESTER), T., 1827; P., 236.
- C₄H₇O₂N₃ α-Triazobutyric acid, and its silver salt, and resolution of (FORSTER and MÜLLER), T., 193.
- α-Triazoisobutyric acid, and its potassium and silver salts (FORSTER and MÜLLER), T., 196.
- C₄H₇O₃N Ethyl formylcarbamate (RUHEMANN and PRIESTLEY), T., 454; P., 62.
- C₄H₇O₃N₃ Ureidomalonamide (WOOD and ANDERSON), T., 982; P., 154.
- C₄H₇O₃Br *d*-β-Bromo-α-methyl-lactic acid (*d*-β-bromo-α-hydroxyisobutyric acid (KAY), T., 562; P., 90.
- C₄H₈ON₄ α- and *l*-α-Triazobutyramide (FORSTER and MÜLLER), T., 194.
- α-Triazoisobutyramide (FORSTER and MÜLLER), T., 197.
- C₄H₉O₃N *d*-β-Amino-α-hydroxyisobutyric acid (*d*-α-methylisoserine), conversion of, into *d*-α-methylglyceric acid (KAY), T., 560; P., 90.
- C₄H₉NPt Trimethylplatonic cyanide (POPE and PEACHEY), T., 576.
- C₄H₁₀OSi Diethylsilicone (MARTIN and KIPPING), T., 313; P., 28.
- C₄H₁₀O₂Ca Calcium ethoxide, and condensations by (PERKIN and PRATT), T., 161; P., 18.
- C₄H₁₀O₄S₂ Dimethyl dithiodiglycollate, preparation of (PRICE and TWISS), T., 1491; P., 211.

4 IV

- C₄H₃O₃N₃S Thiovioluric acid, and its metallic salts (ISHERWOOD), P., 120.
- C₄H₆N₂Br₄Si Substance, from silicon tetrabromide and acetonitrile (REYNOLDS), T., 513.

C₅ Group.

- C₅H₅N Pyridine, relation between constitution and absorption spectra of (PURVIS), T., 294; P., 14.
- C₅H₈O₃ Dimethylpyruvic acid (PERKIN and SIMONSEN), P., 164.
- C₅H₁₀O₅ $\alpha\beta$ -Dihydroxy- γ -methoxybutyric acid, from oxidation of methyl levulose (IRVINE and HYNB), T., 1226; P., 176.
- C₅H₁₃N isoAmylamine, action of, on *cis*- $\alpha\beta$ -dibenzoylstyrene (SMEDLEY), T., 220.

5 III

- C₅H₆O₂N₂ Acetyl derivative of isoinimazolone (FENTON and WILKS), T., 1332.
- C₅H₇O₂N Ethyl cyanoacetate, action of thiocarbimides on (RUHEMANN), T., 117; P., 14; condensation of sodium derivative of, with ketones and aldehydes (HAWORTH), T., 480; P., 76; (GARDNER and HAWORTH), T., 1955; P., 250.
- C₅H₇O₂N₃ α -Triazoisovaleric acid, and its silver salt (FORSTER and MÜLLER), T., 198.
- C₅H₉O₃N Oxime of dimethylpyruvic acid (PERKIN and SIMONSEN), P., 164.
- C₅H₁₀ON₄ α -Triazoisovaleramide (FORSTER and MÜLLER), T., 199.
- C₅H₁₀O₂N₂ Hydrazone of dimethylpyruvic acid (PERKIN and SIMONSEN), P., 164.

5 IV

- C₅H₇O₂NS Ethyl thioacyanoacetate, preparation of (RUHEMANN), T., 119.
- C₅H₁₀ON₂Cl₂ *s*-Diethyldichlorocarbamide (CHATTAWAY and WÜNSCH), T., 133.

C₆ Group.

- C₆H₆ Benzene, space formulæ for (SHIBATA), T., 1450; P., 209.

6 II

- C₆H₄O₂ *p*-Benzoquinone, absorption spectra of, in the state of vapour and in solution; constitution of (HARTLEY and LEONARD), T., 34.
- C₆H₆O₂ Resorcinol, condensation of benzaldehyde with (POPE and HOWARD), P., 304.
Quinol, absorption spectra of (HARTLEY and LEONARD), T., 34.
- C₆H₆O₃ Hydroxymethylfurfuraldehyde, constitution of (FENTON and ROBINSON), T., 1338.
- C₆H₆O₈ Dihydroxydiketoadipic acid (FERRABOSCHI), T., 1252; P., 178.
- C₆H₇N Aniline, cobaltinitrite of (CUNNINGHAM and PERKIN), T., 1565.
 α -Picoline, absorption spectra of, and of its hydrochloride (PURVIS), T., 296; P., 14.
 γ -Picoline, preparation of (FLASCHNER), T., 670.
- C₆H₈O₄ *cyclo*Butane-1:3-dicarboxylic acid, and some of its derivatives (PERKIN and SIMONSEN), T., 1166; P., 178.
- C₆H₈N₂ Adiponitrile, preparation of, and conversion into 1-imino-2-cyanocyclopentane (THORPE), T., 1902; P., 244.
1-Imino-2-cyanocyclopentane (BEST and THORPE), T., 709; P., 93; formation of, from adiponitrile (THORPE), T., 1903; P., 244.
Phenyldiazine, action of potassium hypochlorite, and hypobromite, acetylchloro-amino-2:4-dichlorobenzene, hypobromous acid, and bromine on (CHATTAWAY), T., 1070; P., 147.
- C₆H₉N β -methyl- β -ethylacrylonitrile (GARDNER and HAWORTH), T., 1961.
- C₆H₁₀O 2-Methylcyclopentan-1-one, preparation of (BEST and THORPE), T., 703; P., 93.
- C₆H₁₀O₂ β -Methyl- β -ethylacrylic acid (GARDNER and HAWORTH), T., 1962.

$C_6H_{10}O_3$ Ethyl acetoacetate, action of monochloromethyl ether on the sodium derivative (SIMONSEN and STOREY), T., 2106 ; P., 290 ; anomalous viscosity of (THOLE), P., 198.

Propionic anhydride, preparation of (DENHAM), T., 1238 ; P., 179.

$C_6H_{10}O_4$ Ethyl oxalate, action of Grignard's reagent on (INGLIS and MASON), P., 195.

Adipic acid, formation of 1-phenylpyrrolidine-2:5-dicarboxylic acid from (LE SUEUR), T., 273 ; P., 36.

Methoxy- β -methoxycrotonic acid, and its silver salt (SIMONSEN and STOREY), T., 2109.

$C_6H_{10}O_8$ Mucic acid, oxidation of, in presence of iron (FERRABOSCHI), T., 1248 ; P., 178.

Saccharic acid, oxidation of, in presence of iron (FERRABOSCHI), T., 1252 ; P., 178.

$C_6H_{10}O_{10}$ Dihydroxymucic acid (FERRABOSCHI), T., 1252 ; P., 178.

$C_6H_{11}Br$ Bromocyclohexane, action of, on ethyl sodiomalonate (HOPE and PERKIN), T., 1360 ; P., 207.

$C_6H_{12}O_3$ Ethyl α -hydroxyisobutyrate, preparation of (PARRY), P., 305.

$C_6H_{12}O_6$ Glucose, mutarotation of, and its nitrogen derivatives (GILMOUR), P., 225.

$C_6H_{15}N$ Triethylamine, preparation and crystallography of the picrate and styphtate of (JERUSALEM), T., 1281.

6 III

$C_6HO_7N_5$ 2:3:5-Trinitroquinonediazide (MELDOLA and HAY), T., 1383 ; P., 208.

C_6HNC_6 Hexachloro- α -picoline, absorption spectrum of (PURVIS), T., 298.

$C_6H_2O_4N_4$ Dinitrohydroxyquinonediazide, and its sodium derivative (MELDOLA and HAY), T., 1384.

$C_6H_3O_7N_3$ Picric acid, morphotropic relationships between the derivatives of (JERUSALEM), T., 1275 ; P., 201.

2:3:5-Trinitrophenol, preparation, properties, and metallic derivatives of (MELDOLA and HAY), T., 1382.

$C_6H_3O_8N_3$ Trinitroresorcinol (*styphtic acid*), crystallography of (JERUSALEM), T., 1278.

$C_6H_4O_7N_4$ 2:3:5-Trinitro-4-aminophenol, preparation and properties of (MELDOLA and HAY), T., 1378 ; P., 207.

$C_6H_5O_2N$ Nitrobenzene, reduction of (PERKIN and PRATT), T., 165 ; anomalous viscosity of (THOLE), P., 198.

$C_6H_5O_2Cl$ Chloromethylfurfuraldehyde, new method of preparation of (FENTON and ROBINSON), T., 1339.

$C_6H_5N_2Cl$ Benzenediazonium chloride, determination of the rate of decomposition of (LAMPOUGH), P., 165.

$C_6H_5N_2Br_3$ Tribromophenylhydrazine, preparation and properties of (CHATTAWAY), T., 865 ; P., 120.

$C_6H_6O_2S$ Benzenesulphinic acid, ferric salt, reactions of (THOMAS), T., 343.

C_6H_6NBr *p*-Bromoaniline, cobaltinitrite of (CUNNINGHAM and PERKIN), T., 1566.

C_6H_7ON 2-Cyanocyclopentan-1-one, and its sodium derivative (BEST and THORPE), T., 709 ; P., 93.

$C_6H_7O_4Br_3$ $\alpha\beta$ -Tribromobutane- $\beta\delta$ -dicarboxylic acid (PERKIN and SIMONSEN), T., 1173.

$C_6H_9O_2N$ δ -Cyanovaleric acid, preparation of, and its silver salt (BEST and THORPE), T., 710 ; P., 94.

$C_6H_9O_4Br$ α -Bromobutane- $\beta\delta$ -dicarboxylic acid (PERKIN and SIMONSEN), T., 1174.

- $C_6H_{10}O_2S_2$ Ethyl dithio-oxalate, preparation of (JONES and TASKER), T., 1905 ; P., 247.
- $C_6H_{10}O_4S_2$ Substance, from action of sulphur monochloride on silver propionate (DENHAM), T., 1238.
- $C_6H_{11}ON_3$ Semicarbazone of *cyclopentanone* (BEST and THORPE), T., 702.
- $C_6H_{11}O_2N$ Piperidylformanilide (RUHEMANN), T., 119.
- $C_6H_{11}O_2N_3$ Ethyl α - and *l*- α -triazobutyrate (FORSTER and MÜLLER), T., 194.
Ethyl α -triazoisobutyrate (FORSTER and MÜLLER), T., 197.
- $C_6H_{11}O_2N_3$ Semicarbazone of dimethylpyruvic acid (PERKIN and SIMONSEN), P., 164.
- $C_6H_{15}O_3Sb$ Ethyl antimonite (MACKEY), T., 607 ; P., 98.

6 IV

- $C_6H_2O_2NCl_3$ 2:3:4-Trichloropicolinic acid, absorption spectra of (PURVIS), T., 299.
- $C_6H_3ON_2Cl_3$ 2:3:4-Trichloropicolinamide, absorption spectrum of (PURVIS), T., 298.
- $C_6H_3O_3IS$ 2:3:5-Tri-iodobenzenesulphonic acid (+ 3H₂O), and its metallic salts (BOYLE), T., 1713 ; P., 35.
2:4:5-Tri-iodobenzenesulphonic acid, and its metallic salts (BOYLE), T., 1715 ; P., 35.
3:4:5-Tri-iodobenzenesulphonic acid, and its metallic salts (BOYLE), T., 1710 ; P., 35.
- $C_6H_4O_3IS$ 2:4-Di-iodobenzenesulphonic acid, and its metallic salts (BOYLE), T., 1710 ; P., 35.
2:5-Di-iodobenzenesulphonic acid (and + 3H₂O), and its metallic salts and their solubilities (BOYLE), T., 1701 ; P., 35.
3:4-Di-iodobenzenesulphonic acid (and + H₂O), and its metallic salts (BOYLE), T., 1695 ; P., 35.
3:5-Di-iodobenzenesulphonic acid, and its metallic salts (BOYLE), T., 1704 ; P., 35.
- $C_6H_5O_3IS$ Iodobenzene-*m*-sulphonic acid, sodium salt of (BOYLE), T., 1694.
- $C^*H_5O_5N_2Na_3$ Substance, from tetraketopiperazine and sodium ethoxide (DE MOUILLIED and RULE), T., 550 ; P., 71.
- $C_6H_{18}O_4SPT_2$ Trimethylplatonic sulphate (+ 2H₂O) (POPE and PEACHEY), T., 575.

6 V

- $C_6H_2O_2ClIS$ 2:3:5-Tri-iodobenzenesulphonyl chloride (BOYLE), T., 1714.
2:4:5-Tri-iodobenzenesulphonyl chloride (BOYLE), T., 1716.
3:4:5-Tri-iodobenzenesulphonyl chloride (BOYLE), T., 1712.
- $C_6H_3O_2ClIS$ 2:4-Di-iodobenzenesulphonyl chloride (BOYLE), T., 1710.
2:5-Di-iodobenzenesulphonyl chloride (BOYLE), T., 1703.
3:4-Di-iodobenzenesulphonyl chloride (BOYLE), T., 1697.
3:5-Di-iodobenzenesulphonyl chloride (BOYLE), T., 1707.
- $C_6H_3O_2Cl_2IS$ 2:5-Di-iodobenzene-sulphonyl chloride dichloride (BOYLE), T., 1704.
- $C_6H_3O_3N_2IS$ Diazo-anhydride of iodoaniline-*p*-sulphonic acid (BOYLE), T., 1694.
- $C_6H_4O_2NI_3S$ 2:3:5-Tri-iodobenzenesulphonamide (BOYLE), T., 1714
2:4:5-Tri-iodobenzenesulphonamide (BOYLE), T., 1716.
3:4:5-Tri-iodobenzenesulphonamide (BOYLE), T., 1712.
- $C_6H_4O_5NIS$ 5-Iodo-2-nitrobenzenesulphonic acid, potassium salt of (BOYLE), T., 1700.

- C₆H₅O₂NI₂S** 2:4-Di-iodobenzenesulphonamide (BOYLE), T., 1710.
 2:5-Di-iodobenzenesulphonamide (BOYLE), T., 1704.
 3:4-Di-iodobenzenesulphonamide (BOYLE), T., 1697.
 3:5-Di-iodobenzenesulphonamide (BOYLE), T., 1707.
C₆H₆O₃NIS *m*-Iodoaniline-*p*-sulphonic acid (BOYLE), T., 1709.
p-Iodoaniline-*o*-sulphonic acid (BOYLE), T., 1699.

C₇ Group.

- C₇H₆O** Benzaldehyde, condensation of resorcinol with (POPE and HOWARD), P., 304; oxidation of hydroxy-derivatives of (DAKIN), P., 194.
C₇H₆O₂ Benzoic acid, action of sulphur monochloride on sodium salt of (DENHAM), T., 1237; P., 179.
C₇H₇N Methylenedianiline, action of, on *p*-tolylthiocarbimide (SENIER and SHEPHEARD), T., 505.
C₇H₉N Methylaniline, action of ethylene dibromide on (DUNLOP and JONES), T., 416; P., 61.
m-Toluidine, preparation and crystallography of the picrate of (JERUSALEM), T., 1284.
p-Toluidine, cobaltinitrite of (CUNNINGHAM and PERKIN), T., 1566.
C₇H₁₀O₃ *cyclo*Hexanone-3-carboxylic acid, synthesis of (DOBSON, FERNS, and PERKIN), T., 2010; P., 263.
C₇H₁₁N β -Methyl- β -propylacrylonitrile (GARDNER and HAWORTH), T., 1963.
 $\beta\beta$ -Diethylacrylonitrile (GARDNER and HAWORTH), T., 1965.
C₇H₁₂O 2:5-Dimethylcyclopentan-1-one, preparation of (BEST and THORPE), T., 705; P., 93.
 2-Ethylcyclopentan-1-one (BEST and THORPE), T., 713; P., 93.
C₇H₁₂O₂ β -Methyl- β -propylacrylic acid (GARDNER and HAWORTH), T., 1963.
C₇H₁₂O₃ Ethyl dimethylpyruvate (PERKIN and SIMONSEN), P., 164.
C₇H₁₂O₄ α -Methyladipic acid, formation of, from δ -cyanohectic acid (BEST and THORPE), T., 712; P., 93.
 Ethyl malonate, action of thiocarbimides on (RUHEMANN), T., 117; P., 14; action of bromocyclohexane and of 4-bromo-1-methylcyclohexane on the sodium derivative of (HOPE and PERKIN), T., 1360; P., 207.
C₇H₁₃Br 4-Bromo-1-methylcyclohexane, action of, on ethyl sodiomalonate (HOPE and PERKIN), T., 1360; P., 207.
C₇H₁₄O₆ Methyl laevulose, and its derivatives (IRVINE and HYND), T., 1220; P., 176.

7 III

- C₇H₅O₂N** 3:4-Dihydroxybenzoxonitrile (*protocatechuonitrile*) (EWINS), T., 1488; P., 210.
C₇H₅O₄N 4-Nitro-1:2-methylenedioxybenzene, formation of, from piperonal (SALWAY), T., 1163; (PERKIN, ROBINSON, and THOMAS), T., 1930.
C₇H₅O₅N 5-Nitro-1-hydroxy-2:3-methylenedioxybenzene (SALWAY), T., 1161.
C₇H₅NS Phenylthiocarbimide, action of diphenylmethylenediamine on (SENIER and SHEPHEARD), T., 498.
C₇H₆ON₄ *p*-Triazobenzaldoxime (FORSTER and DUNN), T., 430.
 1-Hydroxy-5-phenyltetrazole (FORSTER), T., 186; P., 25.
C₇H₆OCl Benzhydroxamic chloride, interaction of sodium azide and (FORSTER), T., 184; P., 25.

- C_7H_7ON Benzamide, action of phosphorus pentachloride on (TITHERLEY and WORRALL), T., 1143; P., 150.
- $C_7H_7O_3N$ Trihydroxypyridylacetic acid (BEST and THORPE), T., 1528.
- $C_7H_5O_2S$ *o*-Toluenesulphinic acid, ferric salt, reactions of (THOMAS), T., 343.
p-Toluenesulphinic acid, ferric salt, reactions of (THOMAS), T., 344.
- $C_7H_5O_4N_2$ Glutazylacetic acid (BEST and THORPE), T., 1528.
- C_7H_5ON 2-Cyano-2-methylcyclopentan-1-one (BEST and THORPE), T., 711; P., 93.
- $C_7H_{10}ON_4$ Semicarbazone of 2-cyanocyclopentan-1-one (BEST and THORPE), T., 710.
- $C_7H_{11}O_2N$ δ -Cyanohectic acid, and its silver salt (BEST and THORPE), T. 712.
- $C_7H_{11}O_3N$ 4-Oximinocyclohexanecarboxylic acid, optically active (MILLS and BAIN), P., 177.
- $C_7H_{13}O_2N_3$ Ethyl α -triazoisovalerate (FORSTER and MÜLLER), T., 198.

7 IV

- $C_7H_7O_2NCl_3$ Methyl 2:3:4-trichloropicolinate, absorption spectrum of (PURVIS), T., 299.
- C_7H_7ONCl *m*-Chloroformanilide (DAVIS), T., 1398.
- $C_7H_7O_2NS$ Nitrobenzyl mercaptan (*o*-, *m*-, and *p*-), preparation of (PRICE and TWISS), T., 1725; P., 232.
- $C_7H_7O_2N_2S$ Methanesulphonyl-*p*-phenylenediazoimide (MORGAN and PICKARD), P., 301.
- $C_7H_5O_3SSe$ Benzyl selenosulphuric acid, potassium salt (PRICE and JONES), T., 1729; P., 234.
- $C_7H_5O_4NP$ Benzoylphosphamic acid (TITHERLEY and WORRALL), T., 1153; P., 150.
- $C_7H_9N_4KPt_2$ Potassium trimethylplatonic platinumocyanide (POPE and PEACHEY), T., 576.
- $C_7H_{10}O_2N_2S$ Methanesulphonyl-*p*-phenylenediamine (MORGAN and PICKARD), P., 301.

7 V

- $C_7H_5ONCl_3P$ α -Chlorobenzylidenephosphamic chloride (TITHERLEY and WORRALL), T., 1149; P., 150.
- $C_7H_5O_2NCl_2P$ Benzoylphosphamic chloride (TITHERLEY and WORRALL), T., 1151; P., 150.
- $C_7H_7O_5NSSe$ Nitrobenzyl selenosulphuric acid (*o*-, *m*-, and *p*-), potassium salts (PRICE and JONES), T., 1729; P., 234.

 C_8 Group.

- C_8H_{12} 1:1-Dimethyl- $\Delta^{2,5}$ -cyclohexadiene, the so-called, of Harries and Antouin (CROSSLEY and RENOUF), T., 930; P., 145.

8 II

- $C_8H_6O_2$ Benzoylformaldehyde, refraction of (SMEDLEY), T., 218; P., 17.
- $C_8H_7O_3$ Piperonal, action of nitric acid on (SALWAY), T., 1163.
- $C_8H_6O_5$ 3:4-Dihydroxyphenylglyoxylic acid (+ H_2O) (BARGER and EWINS), T., 560.
- C_8H_8O Acetophenone, oxidation of hydroxy-derivatives of (DAKIN), P., 194.
- $C_8H_8O_2$ Phenylacetic acid, action of sulphur monochloride on silver salt of (DENHAM), T., 1239.

- $C_8H_8O_2$ Toluic acid (*o*-, *m*-, and *p*-), action of sulphur monochloride on silver salts of (DENHAM), T., 1239.
- $C_8H_8O_4$ Mandelic acid, resolution of (KIPPING), T., 414; P., 56; formation of the *d*-acid from amygdalin (TUTIN), T., 667; P., 118; asymmetric synthesis of the *l*-acid (MCKENZIE and HUMPHRIES), T., 1105; P., 164.
- $C_8H_8O_3$ 4-Hydroxy-*o*-toluic acid, reduction of (BAUDISCH, HIBBERT, and PERKIN), T., 1870; P., 249.
- 6-Hydroxy-*o*-toluic acid, reduction of (BAUDISCH and PERKIN), T., 1883; P., 249.
- 5-Hydroxy-*m*-toluic acid, reduction of (MELDRUM and PERKIN), T., 1889; P., 249.
- $C_8H_8O_5$ 3:4-Dihydroxymandelic acid, and its salts (BARGER and EWINS), T., 557.
- C_8H_9N *m*-Aminostyrene, hydrochloride (TUTIN, CATON, and HAM), T., 2125.
- C_8H_9Cl α -Chloro- β -phenylethane, preparation of (BARGER), T., 2194.
- $C_8H_{10}O_2$ Lactone of 1-methyl- Δ^6 -*cyclo*-hexen-4-ol-2-carboxylic acid (BAUDISCH, HIBBERT, and PERKIN), T., 1881.
- $C_8H_{10}O_3$ *cis*-Norpinic anhydride (PERKIN and SIMONSEN), T., 1176.
- $C_8H_{12}O_2$ *cyclo*Hexylideneacetic acid, formation of (HOPE and PERKIN), T., 1366.
- Lactone of *cis*-1-methyl-*cyclo*hexan-2-ol-6-carboxylic acid (BAUDISCH and PERKIN), T., 1888.
- Lactone of *cis*-1-methyl-*cyclo*hexan-3-ol-5-carboxylic acid (MELDRUM and PERKIN), T., 1898; P., 249.
- Dimethyldihydroresorcin, condensation of, with ethylamine (HAAS), T., 421; P., 19.
- $C_8H_{12}O_3$ Ethyl *cyclopentanone*-2-carboxylate, preparation of (DOBSON, FERNS, and PERKIN), T., 2015.
- 1-Methyl*cyclo*hexan-2-one-6-carboxylic acid (BAUDISCH and PERKIN), T., 1886.
- 1-Methyl*cyclo*hexan-3-one-5-carboxylic acid (MELDRUM and PERKIN), T., 1899.
- 1-Methyl- Δ^6 -*cyclo*hexen-4-ol-2-carboxylic acid (BAUDISCH, HIBBERT, and PERKIN), T., 1882; P., 249.
- $C_8H_{12}O_4$ *trans*-Norpinic acid (PERKIN and SIMONSEN), T., 1177.
- $C_8H_{12}O_5$ Pentane- $\alpha\delta\epsilon$ -tricarboxylic acid (+ $\frac{1}{2}H_2O$) (DOBSON, FERNS, and PERKIN), T., 2013.
- $C_8H_{14}O$ Methylheptenone, action of dehydrating and of oxidising agents on (CROSSLEY and RENOUF), T., 935.
- $C_8H_{14}O_2$ *cyclo*Hexylacetic acid (HOPE and PERKIN), T., 1364.
- $C_8H_{14}O_3$ *d*-Amyl pyruvate (MCKENZIE and MÜLLER), T., 545.
- 1-Methyl*cyclo*hexan-2-ol-6-carboxylic acid (*cis*- and *trans*-) (BAUDISCH and PERKIN), T., 1887; P., 249.
- 1-Methyl*cyclo*hexan-3-ol-5-carboxylic acid (*cis*- and *trans*-) (MELDRUM and PERKIN), T., 1897; P., 249.
- 1-Methyl*cyclo*hexan-4-ol-2-carboxylic acid (*cis*- and *trans*-, A and B) (BAUDISCH, HIBBERT, and PERKIN), T., 1877; P., 249.
- $C_8H_{14}O_4$ $\alpha\delta$ -Dimethyladipic acid, preparation of (BEST and THORPE), T., 707.
- α -Ethyladipic acid, formation of, from δ -cyanoheptic acid (BEST and THORPE), T., 714; P., 93.
- Ethyl methoxy- β -methoxy-crotonate (SIMONSEN and STOREY), T., 2109; P., 290.
- $C_8H_{14}O_5$ Methoxymethyl methoxy- β -methoxycrotonate (SIMONSEN and STOREY), T., 2110.

$C_8H_{14}O_6$ Ethyl tartrate, rotation of, in benzaldehyde and in quinoline (PATTERSON and McDONALD), T., 321; P., 36; rotation of, and cryoscopic experiments on (PATTERSON and MONTGOMERIE), T., 1130.

$C_8H_{16}O_6$ Methyl methylfructoside (IRVINE and HYND), T., 1227.

8 III

$C_8H_3O_3N$ 3:4-Carbonyldioxybenzoxitrile (EWINS), T., 1488; P., 210.

$C_8H_5O_2Cl_3$ 3:4-Dichloromethylenedioxybenzyl chloride (EWINS), T., 1485; P., 210.

$C_8H_5O_3N$ 3:4-Methylenedioxyphenylglyoxylonitrile (EWINS), T., 1487; P., 210.

$C_8H_5O_3Cl$ 3:4-Carbonyldioxybenzyl chloride, preparation of (EWINS), T., 1485; P., 210.

$C_8H_6O_4N_4$ 2:3:5-Trinitro-4-acetylaminophenol, interaction of, with amines (MELDOLA and HAY), T., 1033; P., 167; potassium and sodium salts (MELDOLA and HAY), T., 1380.

C_8H_7ON *d*-Benzaldehydecyanohydrin, synthesis of (AULD), T., 927; P., 62. Indoxyl, condensations of, with aldehydes (PERKIN and THOMAS), T., 795; P., 125; oxidation of solutions of (THOMAS, BLOXAM, and PERKIN), T., 842; P., 126.

$C_8H_7O_2Cl$ *d*-Phenylchloroacetic acid, preparation of, and conversion of, into mixtures of *r*- and *l*-mandelic acids, and *r*- and *l*-phenylaminoacetic acids (MCKENZIE and CLOUGH), T., 782.

l-Phenylchloroacetic acid, conversion of, into mixtures of *r*- and *d*-, and *r*- and *l*-mandelic acids, and *r*- and *d*-, and *r*- and *l*-phenylaminoacetic acids (MCKENZIE and CLOUGH), T., 788; P., 70.

o-Chloro-*p*-hydroxyacetophenone, preparation of (TUTIN, CATON, and HANN), T., 2117.

$C_8H_7O_2N$ 5-Nitro-1-methoxy-2:3-methylenedioxybenzene (SALWAY), T., 1161; P., 160.

$C_8H_7O_4N_3$ 3:4:5-Trinitro-*o*-xylene (CROSSLEY and RENOUF), T., 204.

3:4:6-Trinitro-*o*-xylene (CROSSLEY and RENOUF), T., 204.

C_8H_7NS *p*-Tolylthiocarbimide, action of methylenecaniline on (SENIER and SHEPHEARD), T., 505.

$C_8H_8ON_4$ Triazoacetanilide (FORSTER and MÜLLER), T., 201.

$C_8H_8O_4N_2$ 3:4-Dinitro-*o*-xylene (CROSSLEY and RENOUF), T., 204.

3:5-Dinitro-*o*-xylene (CROSSLEY and RENOUF), T., 204.

3:6-Dinitro-*o*-xylene (CROSSLEY and RENOUF), T., 204.

4:5-Dinitro-*o*-xylene (CROSSLEY and RENOUF), T., 204).

$C_8H_8O_2S$ 5-Sulpho-*m*-toluic acid (+2H₂O), and its salts (MELDRUM and PERKIN), T., 1893.

C_8H_8ON Acetanilide, chlorination of (JONES and ORTON), T., 1056; P., 146.

$C_8H_8O_3N$ Phenylaminoacetic acid (*d*- and *l*-), action of nitrous acid on, and conversion of, into phenyl-halogen-acetic acids (MCKENZIE and CLOUGH), T., 791.

d-Mandelamide (WREN), T., 1583; P., 219.

3-Nitro-*o*-xylene (CROSSLEY and RENOUF), T., 204.

4-Nitro-*o*-xylene (CROSSLEY and RENOUF), T., 204.

o-Amino-*p*-hydroxyacetophenone (TUTIN, CATON, and HANN), T., 2120; P., 259.

$C_8H_9O_3N$ 5-Amino-1-methoxy-2:3-methylenedioxybenzene, and its hydrochloride (SALWAY), T., 1162.

$C_8H_9O_3N$ 4-Nitroveratrole, formation of, from vanillin methyl ether (SALWAY), T., 1163.

- $C_8H_{10}O_2N_2$ *p*-Nitrophenylethylamine, and its hydrochloride (BARGER and WALPOLE), T., 1723.
- $C_8H_{10}O_4Br_2$ 1:3-Dibromonorpinic acid (PERKIN and SIMONSEN), T., 1177.
- $C_8H_{11}ON$ *p*-Hydroxyphenylethylamine, isolation and synthesis of (BARGER), T., 1123; P., 162; further syntheses of (BARGER and WALPOLE), T., 1720; P., 229; and its hydrochloride (TUTIN, CATON, and HANN), T., 2123.
- 2-Cyano-2:5-dimethylcyclopentan-1-one (BEST and THORPE), T., 706.
- 2-Cyano-2-ethylcyclopentan-1-one (BEST and THORPE), T., 713.
- $C_8H_{11}O_2N$ α -Cyano- $\beta\beta$ -diethylacrylic acid (GARDNER and HAWORTH), T., 1965.
- β -*p*-Dihydroxy- β -phenylethylamine, and its hydrochloride (TUTIN, CATON, and HANN), T., 2120; P., 289.
- Semicifolinine, salts of (WATT), T., 473; P., 68.
- $C_8H_{11}O_4N$ δ -Cyanobutylmalonic acid, and its silver salt (BEST and THORPE), T., 704.
- $C_8H_{11}O_4Br_3$ Methyl $\alpha\beta\delta$ -tribromo-butane- $\beta\delta$ -dicarboxylate (PERKIN and SIMONSEN), T., 1173.
- $C_8H_{12}ON_4$ Semicarbazone of 2-cyano-2-methylcyclopentan-1-one (BEST and THORPE), T., 711.
- $C_8H_{12}O_2Br_2$ 1:4-Dibromo-1-methylcyclohexane-2-carboxylic acid (BAUDISCH, HIBBERT, and PERKIN), T., 1882.
- $C_8H_{12}O_4Br_2$ Methyl $\alpha\delta$ -dibromoadipate (LE SUEUR), T., 276; P., 36.
- $C_8H_{13}ON_3$ Semicarbazone of 1-methyl- Δ^1 -cyclohexen-3-one (SIMONSEN and STOREY), T., 2112.
- $C_8H_{13}O_2N$ δ -Cyano- α -methylhexoic acid, preparation of, and its silver salt (BEST and THORPE), T., 706.
- δ -Cyanoheptoic acid and its silver salt (BEST and THORPE), T., 713.
- $C_8H_{13}O_2Br$ 4-Bromo-1-methylcyclohexane-2-carboxylic acid (*cis*- and *trans*-A) (BAUDISCH, HIBBERT, and PERKIN), T., 1878.
- 5-Bromo-1-methylcyclohexane-3-carboxylic acid (*cis*- and *trans*-) (MELDRUM and PERKIN), T., 1898.
- cis*-6-Bromo-1-methylcyclohexane-2-carboxylic acid (BAUDISCH and PERKIN), T., 1889.
- $C_8H_{13}O_3N$ 3-Oximino-1-methylcyclohexane-5-carboxylic acid (MELDRUM and PERKIN), T., 1900.
- $C_8H_{14}O_2S_2$ Propyl dithio-oxalate (JONES and TASKER), T., 1906; P., 247.
- $C_8H_{14}O_4S_2$ α -Dithiodibutyric acid, preparation of (PRICE and TWISS), T., 1052; P., 165.
- α -Dithiodisobutyric acid, preparation of (PRICE and TWISS), T., 1054; P., 165.
- $C_8H_{15}ON$ Tropine, affinity values of, and its derivatives (VELEY), T., 1; configuration of (BARROWCLIFF and TUTIN), T., 1966; P., 256.
- ψ -Tropine, configuration of (BARROWCLIFF and TUTIN), T., 1966; P., 256.
- $C_8H_{15}ON_3$ Semicarbazone of 2:5-dimethylcyclopentan-1-one (BEST and THORPE), T., 706.
- Semicarbazone of 2-ethylcyclopentan-1-one (BEST and THORPE), T., 713.
- $C_8H_{16}O_2S$ Diethoxythioxan (CLARKE and SMILES), T., 992; P., 145.
- $C_8H_{20}NBr$ Tetraethylammonium bromide, molecular weight of (SCOTT), T., 1200; P., 173; (THORPE), P., 285.

8 IV

- $C_8H_3O_2NCl_2$ 3:4-Dichloromethylenedioxybenzoxonitrile (EWINS), T., 1487; P., 210.
- $C_8H_6ONCl_2$ Acetylchloroamino-2:4-dichlorobenzene, action on phenylhydrazine (CHATTAWAY), T., 1071; P., 147.

- $C_8H_6O_4N_2Cl_2$ 3:5-Dichloro-4:6-dinitro-*o*-xylene, preparation from 4:6-dinitro-*o*-xylene (CROSSLEY and RENOUF), T., 209.
- $C_8H_7ON_2Cl_3$ Benzyltrichlorocarbamide (CHATTAWAY and WÜNSCH), T., 134.
- $C_8H_7O_2N_2Cl$ Benzoylchlorocarbamide (CHATTAWAY and WÜNSCH), T., 130.
2-Chloro-4-nitrosoacetanilide (CAIN), T., 716; P., 123.
- $C_8H_7O_3I_3S$ Ethyl 2:3:5-tri-iodobenzenesulphonate (BOYLE), T., 1714.
- C_8H_9ONCl Chloroacetanilide, melting-point curves of mixtures of *o*- and *p*- (JONES and ORTON), T., 1059.
- $C_8H_9ON_2Cl_2$ Benzyl-dichlorocarbamide (CHATTAWAY and WÜNSCH), T., 134.
- $C_8H_9O_2NCl$ α -Chloro- β -*p*-nitrophenylethane (BARGER), T., 2196.
- $C_8H_8O_3I_2S$ Ethyl 3:4-di-iodobenzenesulphonate (BOYLE), T., 1698.
- $C_8H_9ON_2Cl$ Benzylchlorocarbamide (CHATTAWAY and WÜNSCH), T., 134.
2-Chloro-1-aminoacetanilide (CAIN), T., 716; P., 123.

C₉ Group.

- $C_9H_6O_3$ 3:4-Methylenedioxyphenylglyoxylic acid, preparation of (BARGER and EWINS), T., 555.
- $C_9H_8O_2$ Cinnamic acid, configuration of (BAKER), P., 223; halogen derivatives of (JAMES and SUDBOROUGH), T., 1538; P., 211.
Phenyl methyl diketone, refraction of (SMEDLEY), T., 218; P., 17.
- $C_9H_8O_4$ Myristicinaldehyde, action of nitric acid on (SALWAY), T., 1159; P., 160; preparation of (SALWAY), T., 1208; P., 175.
- $C_9H_8O_5$ 3:4-Methylenedioxy-mandelic acid, preparation of (BARGER and EWINS), T., 554.
- $C_9H_{10}O_2$ Phenylacetylcarbinol (WREN), T., 1592.
- $C_9H_{10}O_3$ Phenylmethoxyacetic acid, affinity constant of (FINDLAY, TURNER, and OWEN), T., 938; P., 146.
- $C_9H_{10}O_3$ α -Hydroxy- β -phenylpropionic acid, affinity constant of (FINDLAY, TURNER, and OWEN), T., 940; P., 146.
 β -Hydroxy- β -phenylpropionic acid, affinity constant of (FINDLAY, TURNER, and OWEN), T., 941; P., 146.
Vanillin methyl ether, action of nitric acid on (SALWAY), T., 1163.
Acetovanillone (4-hydroxy-3-methoxyacetophenone), isolation of, from *Apo-cynum androsaemifolium* (MOORE), T., 744; P., 85.
- $C_9H_{11}N$ *dl*-Hydrindamine, resolution of (KIPPING), T., 413; P., 56.
- $C_9H_{12}O$ Ketone, from oxidation of terpinene (HENDERSON and CAMERON), T., 974; P., 151.
- $C_9H_{14}O$ 1:1:5-Trimethyl- Δ^4 -cyclohexen-3-one (*isophorone*), and some of its homologues, synthesis of (CROSSLEY and GILLING), T., 19; preparation of (CROSSLEY and GILLING), P., 96.
- $C_9H_{14}O_2$ 1-Methylcyclohexylidene-4-acetic acid, resolution of (PERKIN, POPE, and WALLACH), T., 1789.
- $C_9H_{14}O_4$ *cyclo*hexylmalonic acid, and its potassium salt (HOPE and PERKIN), T., 1363.
- $C_9H_{14}O_5$ *cis*-Hydroxypinic acid, preparation of (PERKIN and SIMONSEN), T., 1175.

9 III

- $C_9H_2O_3Cl_5$ 3:4-Dichloromethylenedioxyphenyldichloroacetyl chloride (BARGER and EWINS), T., 558.
- $C_9H_2O_3Cl_4$ 3:4-Dichloromethylenedioxyphenylchloroacetyl chloride (BARGER and EWINS), T., 556.

- $C_9H_4O_3Cl_2$ 3:4-Carbonyldioxyphenylchloroacetyl chloride (BARGER and EWINS), T., 557.
- $C_9H_4O_2Cl_2$ 3:4-Carbonyldioxyphenyldichloroacetic acid (BARGER and EWINS), T., 559.
- $C_9H_5O_3Cl$ 3:4-Carbonyldioxyphenylchloroacetic acid (BARGER and EWINS), T., 556.
- $C_9H_7ON_3$ Cinnamylcarbimide (*cinnamyl isocyanate*) (FORSTER), T., 433; P., 69.
- $C_9H_7ON_3$ Cinnamoylazoimide, and transformation of, into cinnamyl carbimide (FORSTER), T., 433; P., 69.
- $C_9H_7O_3N$ Indoxylic acid (PERKIN), T., 847; P., 126.
- $C_9H_7O_4Cl$ Myristicinoyl chloride (SALWAY), T., 1161.
- $C_9H_7O_2N$ Nitromyristicinaldehyde (SALWAY), T., 1160; P., 160.
- $C_9H_7O_7N$ Nitromyristicinic acid (SALWAY), T., 1165.
- $C_9H_8O_2Br_2$ $\alpha\beta$ -Dibromo- β -phenylpropionic acid, action of organic bases on (JAMES and SUDBOROUGH), T., 1543.
- $C_9H_9O_2N$ Anisaldehydecyanohydrin, preparation of, and action of hydrogen chloride on (MCCOMBIE and PARRY), T., 584; P., 95.
- $C_9H_9O_3N$ Hippuric acid, condensation with acetone (PERKIN and SIMONSEN), P., 164.
- $C_9H_9O_3N$ Lactone of ethyl hydrogen α cyano- β hydroxy- $\alpha\beta$ -hydro-muconate (BEST and THORPE), T., 1524.
3:4-Methylenedioxymandelamide (BARGER and EWINS), T., 555.
Myristicinamide (+ H_2O) (SALWAY), T., 1161.
- $C_9H_{10}OBr_2$ $\alpha\beta$ -Dibromo-*p*-methoxy- α -phenylethane (TUTIN, CATON, and HANN), T., 2124.
- $C_9H_{10}O_2N_2$ 5-Nitrosoaceto-*o*-toluidide (CAIN), T., 715; P., 123.
6-Nitrosoaceto-*m*-toluidide (CAIN), T., 715; P., 123.
2-Nitrosoaceto-*p*-toluidide (CAIN), T., 715; P., 123.
- $C_9H_{10}O_3N_2$ Ethyl 2-ketotetrahydropyrrolidene-5-cyanoacetate, and its sodium, potassium and silver salts (BEST and THORPE), T., 1532.
Ethyl-2-ketodihydroisopyrrolyl-5-cyanoacetate (BEST and THORPE), T., 1533.
- $C_9H_{11}ON$ Base, from interaction of β -bromo- α -hydroxy-*p*-methoxy- α -phenylethane and ammonia (TUTIN, CATON, and HANN), T., 2125.
- $C_9H_{11}O_2N_3$ Ethyl 2-iminotetrahydro-pyrrolidene-5-cyanoacetate (BEST and THORPE), T., 1530.
- $C_9H_{11}O_3N$ Ethyl 5-cyanocyclopentan-1-one-2-carboxylate, and its potassium and silver derivatives, and ethylation of (BEST and THORPE), T., 701; P., 92.
- $C_9H_{11}O_5N$ Ethyl hydrogen α -cyano- β -keto adipate, and its silver salt (BEST and THORPE), T., 1524.
- $C_9H_{12}O_2N_2$ Ethyl 2-imino-3-cyanocyclopentane-1-carboxylate (THORPE), P., 18; (BEST and THORPE), T., 696; P., 93.
- $C_9H_{12}O_4N_2$ Ethyl hydrogen β -imino- α -cyano adipate, and its silver salt (BEST and THORPE), T., 1534.
- $C_9H_{12}ON$ *p*-Methoxyphenylethylamine, and its hydrochloride (BARGER and WALPOLE), T., 1724; P., 229.
- $C_9H_{12}O_4N$ δ -Cyanomethylbutylmalonic acid, and its silver salt (BEST and THORPE), T., 706.
- $C_9H_{13}O_4Br$ α -Bromocyclohexylmalonic acid (HOPE and PERKIN), T., 1364.
*cis*Bromopicnic acid (PERKIN and SIMONSEN), T., 1175.
- $C_9H_{13}ON_4$ Semicarbazone of 2-cyano-2:5-dimethylcyclopentan-1-one (BEST and THORPE), T., 706.
Semicarbazone of 2-cyano-2-ethylcyclopentan-1-one (BEST and THORPE), T., 713.

- $C_9H_{15}ON$ Oxime of 1:1:5-trimethyl- Δ^4 -cyclohexen-3-one (CROSSLEY and GILLING), T., 25.
 $C_9H_{15}O_3N_3$ Semicarbazone of 1-methylcyclohexan-2-one-6-carboxylic acid (BAUDISCH and PERKIN), T., 1837.
 $C_9H_{21}O_3Sb$ Propyl antimonite (MACKEY), T., 607; P., 98.

9 IV

- $C_9H_{10}ONCl$ *m*-Chloropropionanilide (DAVIS), T., 1398.
 $C_9H_{11}ON_3S_2$ Anhydrodiallyldithiobiuretecarboxylic acid (RUHEMANN and PRIESTLEY), T., 456.
 $C_9H_{10}OCIBr$ α -Chloro- β -bromo-*p*-methoxy- α -phenylethane (TUTIN, CATON, and HANN), T., 2124.
 $C_9H_{11}O_5N_2Na_3$ Substance. from tetraketopiperazine and sodium amyloxide (DE MOUILPIED and RULE), T., 550; P., 71.

 C_{10} Group.

- $C_{10}H_8$ Naphthalene, combustion of, and the atomic weight of carbon (SCOTT), P., 310.
 $C_{10}H_{16}$ Limonene, action of chromyl chloride on (HENDERSON and CAMERON), T., 969; P., 151.
 Pinene, oxidation of, with mercuric acetate (HENDERSON and AGNEW), T., 289; P., 357; conversion of, into sobrerol (HENDERSON and EASTBURN), T., 1465; P., 211.
 Terpinene, action of chromyl chloride on (HENDERSON and CAMERON), T., 969; P., 151.

10 II

- $C_{10}H_8O_7$ Cotarnic acid, synthesis of (PERKIN, ROBINSON, and THOMAS), T., 1977; P., 262.
 $C_{10}H_{10}O$ β -Methylhydrindone, oxidation of (SALWAY and KIPPING), T., 166; P., 16.
 $C_{10}H_{10}O_3$ α -Benzoylpropionic acid (HOPE and PERKIN), T., 2045.
 $C_{10}H_{10}O_4$ *l*-Acetylmandelic acid (+H₂O), hydrolysis of (MCKENZIE and HUMPHRIES), T., 1106.
 $C_{10}H_{10}N_2$ β -Imino- α -cyano- γ -phenylpropane, preparation of, and formation of 1:3-naphthylenediamine from (BEST and THORPE), T., 8.
 1:3-Naphthylenediamine, formation from β -imino- α -cyano- γ -phenylpropane (BEST and THORPE), T., 8.
 $C_{10}H_{12}O$ α -*p*-Tolylpropaldehyde, isolation of, from terpinene (HENDERSON and CAMERON), T., 973; P., 151.
 $C_{10}H_{12}O_2$ Glycide *o*-tolyl ether (BOYD and KNOWLTON), T., 1802; P., 235.
 β -Phenyl- α -methylpropionic acid, resolution of, and rotatory power of the *d*-acid (PICKARD and YATES), T., 1019; P., 152.
 $C_{10}H_{12}O_3$ Acetyl derivative of α -*p*-dihydroxy- α -phenylethane (TUTIN, CATON, and HANN), T., 2124.
 Phenylethoxyacetic acid, affinity constant of (FINDLAY, TURNER, and OWEN), T., 939; P., 146.
 $C_{10}H_{12}O_5$ Ethyl 3:4-dihydroxymandelate (BARGER and EWINS), T., 558.
 Trimethylgallic acid, occurrence in nature of, and silver salt (POWER and MOORE), T., 254.
 $C_{10}H_{13}N$ *dl*-Methylhydrindamine, resolution of (KIPPING), T., 411; P., 55.
 $C_{10}H_{14}O_3$ Camphoric anhydride, new method of preparing (EDGERTON), P., 149.

- $C_{10}H_{14}I_2$ Di-iodocamphor (MARSH and STRUTHERS), T., 1786.
- $C_{10}H_{15}N$ α -Dimethylamino- β -phenylethane (BARGER), T., 2195.
- $C_{10}H_{16}O$ 1:1-Dimethyl-5-ethyl- Δ^4 -cyclohexen-3-one (CROSSLEY and GILLING), T., 28.
- Camphor, absorption spectra of halogen, nitro-, and methyl derivatives of (LOWRY and DESCH), T., 807; P., 13; absorption spectra of sulphonic derivatives of (LOWRY and DESCH), T., 1340; P., 192; physical properties of solid solutions of, and borneol (VANSTONE), T., 595; P., 30; mercury derivatives of (MARSH and STRUTHERS), T., 1777; P., 228.
- $C_{10}H_{16}O_2$ 8-Hydroxycarvotanacetone, preparation of, from pinene (HENDERSON and AGNEW), T., 292; P., 35.
- $C_{10}H_{16}O_3$ Ethyl 1-methylcyclohexan-3-one-5-carboxylate (MELDRUM and PERKIN), T., 1899.
- Pinonic acid, preparation of (PERKIN and SIMONSEN), T., 1174.
- $C_{10}H_{16}O_4$ 1-Methylcyclohexyl-4-malonic acid, and its potassium salt (HOPE and PERKIN), T., 1367.
- Camphoric acid, amides and imides of (WOOTTON), P., 308.
- $C_{10}H_{16}O_5$ 1-Methylcyclohexyl-4-tartronic acid, and its barium salt (HOPE and PERKIN), T., 1368.
- $C_{10}H_{16}O_6$ Senecifolic acid, and its silver salt (WATT), T., 472; P., 68.
- $C_{10}H_{17}N$ β -Methyl- β -hexylacrylonitrile (GARDNER and HAWORTH), T., 1964.
- $C_{10}H_{18}O$ Borneol, physical properties of solid solutions of, and camphor (VANSTONE), T., 595; P., 30.
- Menthone, physical properties of solid solutions of, and menthol (VANSTONE), T., 602; P., 30.
- $C_{10}H_{18}O_2$ β -Methyl- β -hexylacrylic acid (GARDNER and HAWORTH), T., 1964.
- Sobrerol, preparation from pinene (HENDERSON and AGNEW), T., 291; P., 35; conversion of pinene into (HENDERSON and EASTBURN), T., 1465; P., 211.
- $C_{10}H_{20}O$ Menthol, physical properties of solid solutions of, and menthone (VANSTONE), T., 602; P., 30.
- $C_{10}H_{20}O_6$ Tetramethyl levulose, preparation of, from methyl methylfructoside (IRVINE and HYND), T., 1227.

10 III

- $C_{10}H_7O_5N$ 7-Nitro-5:6-methylenedioxy-1-hydrindone (PERKIN, ROBINSON, and THOMAS), T., 1981.
- $C_{10}H_8O_2S$ α -Naphthalenesulphinic acid, ferric salt, reactions of (THOMAS), T., 344.
- β -Naphthalenesulphinic acid, ferric salt, reactions of (THOMAS), T., 344.
- $C_{10}H_8O_7N_2$ ω -2(6)-Dinitro-3-methoxy-4:5-methylenedioxy-styrene (SALWAY), T., 1214.
- $C_{10}H_9ON$ Cinnamaldehydecyanohydrin, action of hydrogen chloride on (McCOMBIE and PARRY), T., 584; P., 95.
- $C_{10}H_9OBr$ Bromo- β -methylhydrindone (SALWAY and KIPPING), T., 170.
- $C_{10}H_9O_3N$ 7-Amino-5:6-methylenedioxy-1-hydrindone (PERKIN, ROBINSON, and THOMAS), T., 1982.
- $C_{10}H_9O_3Cl$ *p*-Hydroxyacetophenone chloroacetate (TUTIN, CATON, and HANN), T., 2117.
- ω -Chloro-*p*-acetoxyacetophenone (TUTIN, CATON, and HANN), T., 2119.
- $C_{10}H_9O_4N$ 3:4-Methylenedioxyphenylglyoxylmethylamide (BARGER and EWINS), T., 556.
- $C_{10}H_9O_6N$ Lactone of trihydroxycarbethoxypyridylacetic acid (BEST and THORPE), T., 1527.

- $C_{10}H_{10}O_2N_2$ Lactam of carbethoxyglutazylacetic acid (BEST and THORPE), T., 1526.
- $C_{10}H_{11}OCl$ *d*- β -Phenyl- α -methylpropionyl chloride (*d*-benzylmethylacetyl chloride), preparation of (PICKARD and YATES), T., 1019.
- $C_{10}H_{11}O_2Cl$ *p*-Methoxyphenylpropionyl chloride (BARGER and WALPOLE), T., 1724.
- $C_{10}H_{12}O_2N_2$ Acetyl-*p*-nitrophenylethylamine (BARGER and WALPOLE), T., 1722; P., 229.
Ethyl 2-keto-1-methyltetrahydropyrrolidene-5-cyanoacetate (BEST and THORPE), T., 1535.
- $C_{10}H_{12}O_6N_2$ Carbethoxyglutazylacetic acid (BEST and THORPE), T., 1526.
Ethyl dihydrogen β -imino- α -cyano-butane- $\alpha\gamma\delta$ -tricarboxylate, and its silver salt (BEST and THORPE), T., 1523.
- $C_{10}H_{12}O_6N_4$ 2,5-Dinitro-4-acetylamino-3-dimethylaminophenol, and its silver salt (MELDOLA and HAY), T., 1048.
- $C_{10}H_{13}ON$ 2- β -Methylaminoethyl-benzaldehyde (PYMAN), T., 1749.
2-Methyl-3:4-dihydroisoquinolinium hydroxide, salts of (PYMAN), T., 1749.
- $C_{10}H_{13}O_2N$ *p*-Methoxyphenylpropionamide (BARGER and WALPOLE), T., 1724; P., 229.
3-Nitrodurene (CAIN), P., 260.
- $C_{10}H_{13}O_2N_3$ Phenylacetylsemicarbazone (WREN), T., 1593.
- $C_{10}H_{13}O_2N$ Ethyl 5-cyano-5-methylcyclopentan-1-one-2-carboxylate (BEST and THORPE), T., 702; P., 93.
Ethyl 3-cyano-2-methoxy- Δ^2 -cyclopentene-1-carboxylate (BEST and THORPE), T., 702.
- $C_{10}H_{14}O_2N_2$ α -Dimethylamino- β -*p*-nitrophenylethane, and its oxalate (BARGER), T., 2195.
- $C_{10}H_{14}O_4N_2$ Ethyl hydrogen α -cyano- β -methyliminoadipate, and its silver salt (BEST and THORPE), T., 1536.
Ethyl β -imino- α -cyanoglutarate, preparation of (BEST and THORPE), T., 1518.
- $C_{10}H_{14}O_4Br_2$ Methyl 1:3-dibromo-norpinate (PERKIN and SIMONSEN), T., 1177.
- $C_{10}H_{15}ON$ Iminocamphor, aryl derivatives of (FORSTER and THORNLEY), T., 942; P., 145.
Hordenine, synthesis of (BARGER), T., 2193; P., 289.
- $C_{10}H_{15}ON_3$ Semicarbazone of ketone from oxidation of terpinene (HENDERSON and CAMERON), T., 974; P., 151.
- $C_{10}H_{15}O_2N$ β -Amino- β' -*o*-tolyloxyisopropyl alcohol, and its salts (BOYD and KNOWLTON), T., 1804; P., 235.
- $C_{10}H_{15}O_4Br$ α -Bromo-1-methylcyclohexyl-4-malonic acid (HOPE and PERKIN), T., 1367.
- $C_{10}H_{16}O_2N_2$ 4-Oximino-5-ethylimino-1:1-dimethylcyclohexan-3-one (and + 2H₂O) (HAAS), T., 423.
- $C_{10}H_{16}O_4Br_2$ Ethyl $\alpha\delta$ -dibromoadipate, liquid form of (LE SUEUR), T., 275; P., 36.
- $C_{10}H_{17}ON$ 5-Ethylimino-1:1-dimethyl- Δ^3 -cyclohexen-3-ol, and its hydrochloride and platinichloride (HAAS), T., 422.
- $C_{10}H_{17}ON_3$ Semicarbazone of 1:1:5-trimethyl- Δ^4 -cyclohexen-3-one (CROSSLLEY and GILLING), T., 24.

$C_{10}H_5O_5N_2Na_3$ Substance, from tetraketopiperazine and sodium phenoxide (DE MOULPIED and RULE), T., 551; P., 71.

- $C_{10}H_6O_2NCl_3$ Trichlorobenzoyllactonitrile (FRANCIS and DAVIS), T., 1407.
- $C_{10}H_{10}N_2Br_4Si$ Substance, from silicon tetrabromide and pyridine (REYNOLDS), T., 513.
- $C_{10}H_{14}OI_2Hg_2$ Dimericamphor diiodide (MARSH and STRUTHERS), T., 1783.
- $C_{10}H_{15}OClHg$ Mercuricamphor chloride (MARSH and STRUTHERS), T., 1785.
- $C_{10}H_{15}OBrHg$ Mercuricamphor bromide (MARSH and STRUTHERS), T., 1784.
- $C_{10}H_{15}OIHg$ Mercuricamphor iodide, and its mercuri-iodide (MARSH and STRUTHERS), T., 1784.

10 V

- $C_{10}H_{21}O_3I_2SHg$ Substance, from diethoxythioxan, ethyl iodide and mercuric iodide (CLARKE and SMILES), T., 1003.

 C_{11} Group.

- $C_{11}H_{10}O_2$ Ethyl phenylpropionate, action of, on monoarylcaramides (RUHEMANN), T., 1609; P., 220.
 Δ^3 -Dihydro-2-naphthoic acid, resolution of, and the *d*-acid and its sodium salt (PICKARD and YATES), T., 1014; P., 152.
- $C_{11}H_{10}O_4$ Methoxymethylenedioxy- α -hydrindone (SALWAY), T., 1210.
- $C_{11}H_{10}O_5$ 3-Methoxy-4:5-methylenedioxy-cinnamic acid, and action of nitric acid on (SALWAY), T., 1209.
- $C_{11}H_{12}O$ 1:1-Dimethyl-3-methylenephthalan (SHIBATA), T., 1453; P., 209.
- $C_{11}H_{12}O_2$ Phenylallylacetic acid, resolution of, and the *d*-acid and its salts (PICKARD and YATES), T., 1016; P., 152.
- $C_{11}H_{12}O_3$ α -Benzoylbutyric acid (HOPE and PERKIN), T., 2047.
Ethyl benzoylacetate (HOPE and PERKIN), T., 2042; P., 296.
- $C_{11}H_{12}O_5$ β -3-Methoxy-4:5-methylenedioxypropionic acid (SALWAY), T., 1209.
Ethyl 3:4-methylenedioxy-mandelate (BARGER and EWINS), T., 554.
- $C_{11}H_{12}N_2$ 1-Cyano-2-methyltetrahydroisoquinoline (PYMAN), T., 1750.
- $C_{11}H_{14}O_2$ Phenylpropylacetic acid, resolution of, and the *d*-acid and its salts (PICKARD and YATES), T., 1017; P., 152.
 β -Phenyl- α -ethylpropionic acid, resolution of, and the *d*-acid and its salts (PICKARD and YATES), T., 1018; P., 152.
- $C_{11}H_{14}O_3$ Phenylpropoxyacetic acid, affinity constant of (FINDLAY, TURNER, and OWEN), T., 940; P., 146.
- $C_{11}H_{14}O_6$ Methyl 1:1-dimethylcyclopentan-3:4-dione-2:5-dicarboxylate, preparation of (THORPE), P., 94.
- $C_{11}H_{16}O_2$ Oxymethylenecamphor, condensation with primary and secondary amino-compounds (POPE and READ), T., 171; P., 18.
- $C_{11}H_{18}O$ 1:1-Dimethyl-5-propyl- Δ^4 -cyclohexen-3-one (CROSSLEY and GILLING), T., 29.

11 III

- $C_{11}H_9O_2N$ Lactone of α -cyano- γ -hydroxy- γ -phenylbutyric acid (HAWORTH), T., 483.
- $C_{11}H_9O_4N$ 2-Keto-8(5)-methoxy-6:7-methylenedioxy-1:2-dihydroquinoline (+ $\frac{1}{2}H_2O$), and its hydrochloride, and reduction products (SALWAY), T., 1216.
- $C_{11}H_9O_4Cl_3$ Ethyl 3:4-dichloromethylenedioxyphenylchloroacetate (BARGER and EWINS), T., 558.

- $C_{11}H_9O_5Cl$ Ethyl 3:4-carbonyldioxyphenylchloroacetate (BARGER and EWINS), T., 558.
- $C_{11}H_9O_7N$ 2(6)-Nitro-3-methoxy-4:5-methylenedioxy-cinnamic acid (SALWAY), T., 1215.
- $C_{11}H_{10}O_2N_2$ β -Imino- α -cyano- γ -phenylbutyric acid, and its silver salt (BEST and THORPE), T., 12.
- 1:3-Naphthylenediamine-2-carboxylic acid (BEST and THORPE), T., 12.
- $C_{11}H_{10}O_4N$ Substance, $(C_{11}H_{10}O_4N)_x$, from reduction of 2-keto-8(5)-methoxy-6:7-methylenedioxy-1:2-dihydroquinoline (SALWAY), T., 1217.
- $C_{11}H_{11}ON_5$ Triazoantipyrine (4-triazo-1-phenyl-2:3-dimethylpyrazolone) (FORSTER and MÜLLER), T., 2072; P., 291.
- $C_{11}H_{11}O_3N$ Carbethoxymandelonitrile (FRANCIS and DAVIS), T., 1409.
- $C_{11}H_{11}O_4N$ Oxime of methoxymethylenedioxy- α -hydrindone (SALWAY), T., 1210.
- $C_{11}H_{11}O_5N$ 6-Nitro-5:6-dimethoxy-1-hydrindone (PERKIN, ROBINSON, and THOMAS), T., 1980.
- $C_{11}H_{13}O_2N$ 6:7-Dimethoxy-3:4-dihydroisoquinoline, and its hydrochloride and picrate (PYMAN), T., 1618; P., 217.
- $C_{11}H_{13}O_3N$ Ethyl phenylacetylcarbanic acid (RUHEMANN and PRIESTLEY), T., 452.
- 2-Amino-5:6-dimethoxy-1-hydrindone, hydrochloride and platinumchloride (ROBINSON), T., 2173; P., 296.
- $C_{11}H_{13}O_4N$ 3:4-Methylenedioxyphenylhydroxyacetiminoethyl ether, hydrochloride of (BARGER and EWINS), T., 554.
- $C_{11}H_{15}ON$ *n*-Butyro-*o*-toluidide (DAVIS), T., 1398.
- n*-Butyro-*p*-toluidide (DAVIS), T., 1398.
- Cyanocarone (CLARKE and LAPWORTH), P., 307.
- $C_{11}H_{15}O_3N$ Ethyl 5-cyano-2:5-dimethylcyclopentan-1-one-2-carboxylate (BEST and THORPE), P., 705; P., 93.
- Ethyl 5-cyano-5-ethylcyclopentan-1-one-2-carboxylate (BEST and THORPE), T., 707; P., 93.
- Ethyl 3-cyano-2-ethoxy- Δ^3 -cyclopentene-1-carboxylate (BEST and THORPE), T., 707; P., 93.
- $C_{11}H_{15}ON_3$ Semicarbazone of 1:1-dimethyl-5-ethyl- Δ^4 -cyclohexen-3-one (CROSSLEY and GILLING), T., 28.

C₁₂ Group.

- $C_{12}H_{10}O_2$ Benzylfurfuraldehyde (FENTON and ROBINSON), T., 1335; P., 193.
- $C_{12}H_{10}O_4$ Quinhydrone, absorption spectra of (HARTLEY and LEONARD), T., 34.
- $C_{12}H_{10}O_5$ Acetyl- β -methylæsculetin (POWER and MOORE), T., 256; P., 27.
- $C_{12}H_{12}O_2$ β -Styryl- β -methylacrylic acid (HAWORTH), T., 485.
- $C_{12}H_{13}N_3$ Phenylhydrazone of 2-cyanocyclopentan-1-one (BEST and THORPE), T., 710.
- $C_{12}H_{14}O_2$ Diethylphthalide, formation from magnesium alkyl halides and dimethyl or diethyl phthalate (SHIBATA), T., 1455.
- $C_{12}H_{16}O_5$ *d*-Amyl gallate (MCKENZIE and MÜLLER), T., 548.
- iso*Amyl gallate (MCKENZIE and MÜLLER), T., 547.
- $C_{12}H_{18}O_3$ Ethyl 1:1-dimethyl- Δ^4 -cyclohexen-3-one-5-acetate (CROSSLEY and GILLING), T., 23.
- $C_{12}H_{18}O_5$ Ethyl cyclohexanone-3:6-dicarboxylate (DOBSON, FERNS, and PERKIN), T., 2013; P., 263.
- $C_{12}H_{20}O_3$ Ethyl pinonate (PERKIN and SIMONSEN), T., 1174.
- $C_{12}H_{20}O_4$ Ethyl *cis*-norpinate (PERKIN and SIMONSEN), T., 1176.

- $C_{12}H_{20}O_6$ Levulosediacetone, constitution of (IRVINE and HYND), T., 1220 ; P., 176.
 $C_{12}H_{22}N_2$ 3:5-Diethylimino-1:1-dimethylcyclohexane, and its platinumchloride (HAAS), T., 422.

12 III

- $C_{12}H_{11}ON_3$ *p*-Aminobenzeneazophenol, and its hydrochlorides and their absorption spectra (HEWITT and THOMAS), T., 1294 ; P., 190.
 $C_{12}H_{11}O_2N$ Anhydride of α -benzoylamino- β -dimethylacrylic acid (PERKIN and SIMONSEN), P., 164.
 Benzylfurfuraldehydeoxime (*syn* and *anti*) (FENTON and ROBINSON), T., 1336 ; P., 193.
 $C_{12}H_{11}O_3N$ Ethyl phenylpropiolylcarbamie acid (RUHEMANN and PRIESTLEY), T., 451 ; P., 62.
 $C_{12}H_{11}O_4N$ 2-Keto-8(5)-methoxy-6:7-methylenedioxy-1-methyl-1:2-dihydroquinoline (SALWAY), T., 1218.
 8(5)-Methoxy-6:7-methylenedioxy carbostyryl methyl ether (SALWAY), T., 1218.
 $C_{12}H_{11}O_7N$ Methyl 2(6)-nitro-3-methoxy-4:5-methylenedioxy cinnamate (SALWAY), T., 1215.
 $C_{12}H_{12}ON_4$ Styrylpyrazolecarboxylic acid hydrazide (RUHEMANN), T., 117.
 $C_{12}H_{12}O_2N_2$ Methyl β -imino- α -cyano- γ -phenylbutyrate (BEST and THORPE), T., 10.
 Methyl 1:3-naphthylenediamine-2-carboxylate, and its hydrochloride (BEST and THORPE), T., 11.
 $C_{12}H_{13}O_3N$ α -Benzoylamino- β -dimethylacrylic acid (PERKIN and SIMONSEN), P., 164.
 $C_{12}H_{13}O_4N$ 1-Phenylpyrrolidine-2:5-dicarboxylic acid, formation of, from adipic acid, and its barium, and silver salts (LE SUEUR), T., 273 ; P., 36.
 Oxyisocotarnine (2-Keto-8(5)-methoxy-6:7-methylenedioxy-1-methyl-1:2:3:4-tetrahydroquinoline) (SALWAY), T., 1219 ; P., 175.
 $C_{12}H_{13}O_5N$ Methyl 2(6)-amino-3-methoxy-4:5-methylenedioxy cinnamate (SALWAY), T., 1215.
 $C_{12}H_{13}N_3Si$ Substance, from silicochloroform and potassium pyrrole (REYNOLDS), T., 511.
 $C_{12}H_{14}O_5N_2$ Ethyl 2-keto-4-carbethoxydihydroisopyrrolidyl-5-cyanoacetate (BEST and THORPE), T., 1520.
 Ethyl 2-keto-4-carbethoxytetrahydropyrrolidene-5-cyanoacetate, and its silver salt (BEST and THORPE), T., 1521.
 $C_{12}H_{15}ON$ Anilide of β -methyl- β -ethylacrylic acid (GARDNER and HAWORTH), T., 1962.
 $C_{12}H_{15}O_3N$ 1-Keto-6:7-dimethoxy-2-methyltetrahydroisquinoline (PYMAN), T., 1272 ; P., 190.
 $C_{12}H_{15}O_4N$ Cotarnine, synthesis of substances allied to (SALWAY), T., 1204 ; P., 175.
 $C_{12}H_{15}O_4N_3$ Ethyl 2-imino-4-carbethoxytetrahydropyrrolidene-5-cyanoacetate, and its hydrochloride (BEST and THORPE), T., 1519.
 $C_{12}H_{16}O_4N_2$ Ethyl $\alpha\delta$ -dicyano adipate (BEST and THORPE), T., 696 ; P., 92.
 $C_{12}H_{17}ON$ 3-Cyano-1:2:4-trimethyl-4-ethyl- $\Delta^{1:3}$ -cyclohexadien-6-ol (GARDNER and HAWORTH), T., 1960.
 $C_{12}H_{17}O_2N$ 6:7-Dimethoxy-2-methyltetrahydroisquinoline, and its salts (PYMAN), T., 1273 ; P., 190.
 $C_{12}H_{17}O_3N$ 4:5-Dimethoxy-2- β -methylaminoethylbenzaldehyde (PYMAN), T., 1270 ; P., 190.

- $C_{12}H_{17}O_3N$ 6:7-Dimethoxy-2-methyl-3:4-dihydroisoquinolinium hydroxide, chloride, bromide, aurichloride, and picate (PYMAN), T., 1271; P., 190.
- $C_{12}H_5O_3N_4$ Semicarbazone of ethyl 5-cyano-2:5-dimethylcyclopentan-1-one-2-carboxylate (BEST and THORPE), T., 705.
- $C_{12}H_{20}ON_3$ Semicarbazone of 1:1-dimethyl-5-propyl- Δ^4 -cyclohexen-3-one (CROSSLEY and GILLING), T., 29.
- $C_{12}H_{22}O_2S_2$ *iso*Amyl dithio-oxalate (JONES and TASKER), T., 1906; P., 247.
- $C_{12}H_{22}O_2S_2$ Diethyl α -dithiodibutyrate (PRICE and TWISS), T., 1052; P., 165.
Diethyl α -dithiodiisobutyrate, preparation of (PRICE and TWISS), T., 1054; P., 165.
- $C_{12}H_{26}O_2S$ Acetal sulphide, molecular refraction of, and mercurichloride (CLARKE and SMILES), T., 1000; P., 145.
- $C_{12}H_{27}O_3Sb$ *iso*Butyl antimonite (MACKEY), T., 607; P., 98.

12 IV

- $C_{12}H_9O_9N_5S$ Tetranitrodiphenylamine-*o*-sulphoxide, and its sodium derivatives (BARNETT and SMILES), T., 1257; P., 195.
Tetranitrophenazothionium hydroxide, reactions and sodium derivative of (BARNETT and SMILES), T., 1259; P., 195.
- $C_{12}H_9O_{10}N_5S$ Sulphone, from oxidation of tetranitrophenazothionium hydroxide (BARNETT and SMILES), T., 1261.
- $C_{12}H_7O_5N_3S$ 3:9-Dinitrophenazothionium hydroxide (BARNETT and SMILES), T., 1261.
*iso*Dinitrophenazothionium hydroxide (and + H_2O) (BARNETT and SMILES), T., 1264; P., 195.
- $C_{12}H_7O_6N_3S$ Substance (+ H_2O), from oxidation of dinitroazothionium hydroxide (BARNETT and SMILES), T., 1264.
- $C_{12}H_8O_4N_2S$ 3-Nitro-9-hydroxyphenazothionium hydroxide (BARNETT and SMILES), T., 1262.
- $C_{12}H_8NCIS$ Phenazothionium chloride (+ H_2O) (BARNETT and SMILES), T., 1265; P., 195.
- $C_{12}H_9ONS$ Diphenylamine *o*-sulphoxide (BARNETT and SMILES), T., 1265; P., 195.
- $C_{12}H_{12}N_2CIS$ Diaminothionine chloride (+ $2H_2O$), and platinumchloride (BARNETT and SMILES), T., 1259.

12 V

- $C_{12}H_8O_2NI_3S$ 2:4:5-Tri-iodobenzenesulphonanilide (BOYLE), T., 1716.
3:4:6-Tri-iodobenzenesulphonanilide (BOYLE), T., 1713.

 C_{13} Group.

- $C_{13}H_{10}O_9$ Tannic acid, iodometric estimation of, and action of reducing agents on (GARDNER and HODGSON), T., 1819.
- $C_{13}H_{12}O_2$ Tolylmethylfurfuraldehyde (FENTON and ROBINSON), T., 1338.
- $C_{13}H_{14}N_2$ Diphenylmethylenediamine, action of, on phenylthiocarbimide (SENIER and SHEPHEARD), T., 498.
- $C_{13}H_{16}O_3$ Ethyl α -benzoylisobutyrate (HOPE and PERKIN), T., 2046.
d-Amyl phenylglyoxylate (*d*-*amyl benzoylformate*) (MCKENZIE and MÜLLER), T., 546.
- $C_{13}H_{18}O_2$ Glycide thymyl ether (BOYD and MARLE), T., 1800; P., 235.
- $C_{13}H_{20}O_2$ Ethyl 1:1-dimethyl- Δ^4 -cyclohexen-3-one-5-propionate, hydrolysis of (CROSSLEY and GILLING), T., 28.

- $C_{13}H_{20}O_6$ Ethyl α -diacetylglutarate (SIMONSEN and STOREY), T., 2111; P., 290.
 $C_{13}H_{22}O_4$ Ethyl *cyclohexylmalonate* (HOPE and PERKIN), T., 1363; P., 207.
 $C_{13}H_{22}O_5$ Ethyl *cishydroxypinate* (PERKIN and SIMONSEN), T., 1176.
 $C_{13}H_{22}O_6$ Methyl α -levulosediacetone (IRVINE and HIND), T., 1223; P., 176.

13 III

- $C_{13}H_{11}O_2N$ α -Cyano- β -styryl- β -methylacrylic acid (HAWORTH), T., 485.
 Salicylidene-*m*-aminophenol (SENIER and SHEPHEARD), T., 1947.
 $C_{13}H_{12}ON_2$ Benzoyl-*p*-phenylenediamine, hydrochloride of (MORGAN and ALCOCK), T., 1323; P., 202.
 $C_{13}H_{10}O_2N_2$ 2-Cyano-5-carbanilino*cyclopentan-1-one* (BEST and THORPE), T., 701.
 $C_{13}H_{10}O_3N_4$ *o*-, *m*-, and *p*-Nitrobenzenediazohydroxylamino-*p*-toluene (GEBHARD and THOMPSON), T., 774.
 $C_{13}H_{13}O_2N$ Ethyl α -cyano- α -styrylacetate (HAWORTH), T., 482.
 $C_{13}H_{13}O_3N$ α -Carboxyamino- β -styryl- β -methylacrylic acid (HAWORTH), T., 485.
 $C_{13}H_{13}O_4P$ Phenyl-*p*-tolylphosphoric acid (LUFF and KIPPING), T., 2001.
 $C_{13}H_{13}O_7N$ Ethyl 2(6)-nitro-3-methoxy-4:5-methylenedioxy*cinnamate* (SALWAY), T., 1215.
 $C_{13}H_{16}O_2N_2$ 1-Cyano-6:7-dimethoxy-2-methyltetrahydro*isoquinoline* (PYMAN), T., 1272; P., 190.
 $C_{13}H_{16}O_5N_2$ Ethyl 2-keto-4-carbethoxy-1-methyltetrahydropyrrolidene-5-cyanoacetate (BEST and THORPE), T., 1529.
 $C_{13}H_{16}O_6N_4$ 2:5-Dinitro-4-acetylamino-3-piperidylphenol (MELDOLA and HAY), T., 1049.
 $C_{13}H_{17}O_3N$ 1-Keto-6:7-dimethoxy-2-ethyltetrahydro*isoquinoline* (PYMAN), T., 1746.
 $C_{13}H_{17}O_7N$ Glucose-*o*-carboxyanilide (+ H_2O), and its sodium salt (IRVINE and GILMOUR), T., 1553; P., 219.
 $C_{13}H_{18}O_2N_2$ 6-Imino-3-cyano-1:2:4-trimethyl-4-ethyl- Δ^1 -*cyclohexene-3-carboxylic acid* (GARDNER and HAWORTH), T., 1959.
 $C_{13}H_{18}O_2N$ 6:7-Dimethoxy-2-ethyltetrahydro*isoquinoline*, and its hydrochloride (PYMAN), T., 1746.
 $C_{13}H_{19}O_2N_3$ Phenylhydrazone of 2:3-diketo-4-phenyl-5-anisylpyrroline (RUHEMANN), T., 1608.
 $C_{13}H_{19}O_3N$ 4:5-Dimethoxy-2- β -ethylaminoethylbenzaldehyde (PYMAN), T., 1745.
 6:7-Dimethoxy-2-ethyl-3:4-dihydro*isoquinolinium* hydroxide, chloride, aurichloride, and picate of (PYMAN), T., 1745.
 $C_{13}H_{19}O_5N$ Glucose-*p*-toluidide (and + $\frac{1}{2}H_2O$ and + H_2O), crystalline forms of, and reactions of (IRVINE and GILMOUR), T., 1546; P., 219.
 $C_{13}H_{21}O_3N_3$ Semicarbazone of ethyl 1:1-dimethyl- Δ^4 -*cyclohexen-3-one-5-acetate* (+ $\frac{1}{2}EtOH$) (CROSSLEY and GILLING), T., 24.
 $C_{13}H_{21}O_4Br$ Ethyl α -bromo*cyclohexylmalonate* (HOPE and PERKIN), T., 1364.
 $C_{13}H_{23}ON$ Propionobornylamide (FRANKLAND and BARROW), T., 2025; P., 263.

13 IV

- $C_{13}H_{10}ONCl$ Salicylidene(*o*-, *m*-, and *p*-)chloroaniline (SENIER and SHEPHEARD), T., 1946.
 $C_{13}H_{10}ON_2Cl$ Benzoyl-*p*-aminobenzenediazonium chloride (MORGAN and ALCOCK), T., 1323; P., 202.

- $C_{13}H_{10}O_4N_6S_2$ Methanedisulphonylbis-*p*-phenylenediazoimide (MORGAN and PICKARD), P., 301.
- $C_{13}H_{10}O_5N_3Cl$ Benzoyl-*p*-aminobenzenediazonium perchlorate (MORGAN and ALCOCK), T., 1324; P., 202.
- $C_{13}H_{11}O_2N_2P$ Phenyliminophosphoryl benzamide (TITHERLEY and WORRALL), T., 1152; P., 150.
- $C_{13}H_{11}O_2N_3S$ Toluene- ω -sulphonyl-*p*-phenylenediazoimide (MORGAN and PICKARD), P., 301.
- $C_{13}H_{12}ON_3Br$ *o*-, *m*-, and *p*-Bromobenzenediazohydroxylamino-*p*-toluene (GEBHARD and THOMPSON), T., 775.
- $C_{13}H_{12}O_3ClP$ Phenyl-*p*-tolylphosphoryl chloride (LUFF and KIPPING), T., 2000.
- $C_{13}H_{14}O_2N_2S$ Toluene- ω -sulphonyl-*p*-phenylenediamine (MORGAN and PICKARD), P., 301.
- $C_{13}H_{15}O_3N_2P$ Anilino-*p*-toluidinophosphoric acid, and its alkaloidal salts (LUFF and KIPPING), T., 1998.
- $C_{13}H_{16}O_4N_4S_2$ Methanedisulphonylbis-*p*-phenylenediamine (MORGAN and PICKARD), P., 301.

13 V

- $C_{13}H_{12}O_3N_2ClP$ Benzoylaminoanilinophosphoryl chloride (TITHERLEY and WORRALL), T., 1152; P., 150.

 C_{14} Group.

- $C_{14}H_{10}O_2$ Benzil, physical properties of solid solutions of, and benzoin (VANSTONE), T., 600; P., 30.
- $C_{14}H_{12}O_2$ Benzoin, physical properties of solid solutions of, and benzil (VANSTONE), T., 600; P., 30.
- d*-Benzoin (WREN), T., 1583; P., 219.
- $C_{14}H_{14}S_2$ Benzyl disulphide, preparation of (PRICE and TWISS), T., 1490; P., 211.
- $C_{14}H_{14}Se_2$ Benzyl diselenide (PRICE and JONES), T., 1729; P., 234.
- $C_{14}H_{18}O_3$ Ethyl α -benzoyl- α -methylbutyrate (HOPE and PERKIN), T., 2050.
- $C_{14}H_{24}O_3$ Ethyl α :1:1-dimethyl- Δ^4 -cyclohexen-3-one-5-butyrate, and hydrolysis of (CROSSLEY and GILLING), T., 28.
- $C_{14}H_{24}O_4$ Ethyl 1-methylcyclohexyl-4-malonate (HOPE and PERKIN), T., 1367.
- $C_{14}H_{24}O_5$ Ethyl α -methoxycyclohexylmalonate (HOPE and PERKIN), T., 1366.
- $C_{14}H_{24}O_6$ Ethyl pentane- $\alpha\delta\epsilon$ -tricarboxylate, preparation of (DOBSON, FERNS, and PERKIN), T., 2012.

14 III

- $C_{14}H_9O_8N_6$ Trinitrohydroxy-1-*o*-, *m*-, and *p*-hydroxyphenylmethylbenzimidazole (MELDOLA and HAY), T., 1045.
- $C_{14}H_{10}ON_4$ Benzoyl-*p*-aminodiazobenzene cyanide (MORGAN and ALCOCK), T., 1324.
- $C_{14}H_{10}O_2N$ 1-Benzoyloxy-5-phenyltetrazole (FORSTER), T., 188; P., 25.
- $C_{14}H_{16}O_2S_2$ Phenyl dithio-oxalate (JONES and TASKER), T., 1905; P., 247.
- $C_{14}H_{16}O_4S_2$ Substance, from action of sulphur monochloride on sodium benzoate (DENHAM), T., 1237.
- $C_{14}H_{10}O_8N_4$ Dinitrohydroxy-1-*o*-, *m*-, and *p*-hydroxyphenylmethylbenzimidazole (MELDOLA and HAY), T., 1044.

- $C_{14}H_{11}ON$ 2-(or 4-)Methylacridone (SENIER and SHEPHEARD), T., 444.
Phenylbenzometoxazone, action of phosphorus pentachloride on (TITHERLEY and HICKS), T., 915; P., 95.
- $C_{14}H_{11}O_3N$ Salicylidene-*p*-aminobenzoic acid, and its salts (SENIER and SHEPHEARD), T., 1948.
- $C_{14}H_{12}ON_2$ Methylene-diphenylcarbamide (SENIER and SHEPHEARD), T., 504.
- $C_{14}H_{12}O_2N_2$ 4-Nitroso-4'-acetylaminodiphenyl (CAIN), T., 717; P., 123.
- $C_{14}H_{12}O_3N_2$ (3- and 5-) Nitrosalicylidene-*m*-toluidine (SENIER and SHEPHEARD), T., 1953.
- $C_{14}H_{12}O_4N_2$ $\alpha\alpha'$ -Dicyano- β -benzylglutaric acid, and its silver salt (HAWORTH), T., 484.
- $C_{14}H_{13}ON$ Salicylidene-*m*-toluidine, a new phototropic compound (SENIER and SHEPHEARD), T., 443, 1945; P., 61.
m- and *p*-Hydroxybenzylidene-*m*-toluidine (SENIER and SHEPHEARD), T., 1951.
- $C_{14}H_{13}O_2N$ 7-Benzoin- α -oxime, and its mutarotation (WREN), T., 1587.
Salicyl-*m*-toluidide (SENIER and SHEPHEARD), T., 444.
- $C_{14}H_{13}O_2N_3$ *p*-Acetylaminobenzeneazophenol (HEWITT and THOMAS), T., 1294; P., 190.
- $C_{14}H_{13}ON_2$ *as*-Benzoylmethyl-*p*-phenylenediamine (MORGAN and ALCOCK), T., 1322; P., 202.
Acetylbenzidine, preparation of (CAIN), T., 716; P., 123.
- $C_{14}H_{13}OS$ Benzyl sulphoxide; a possible example of dynamic isomerism (SMYTHE), T., 349.
- $C_{14}H_{13}O_2N_2$ 2-Cyano-5-carbanilino-2-methylcyclopentan-1-one (BEST and THORPE), T., 703.
- $C_{14}H_{15}ON_3$ Dimethylaminobenzeneazophenol, and its absorption spectra, and hydrochloride (HEWITT and THOMAS), T., 1295; P., 190.
o-, *m*-, and *p*-Tolyldiazohydroxylamino-*p*-toluene (GEBHARD and THOMPSON), T., 772.
- $C_{14}H_{16}O_3N_2$ Ethyl 2:6-dicyano-1:1:5-trimethyl- $\Delta^{2:4}$ -cyclohexadien-3-ol-6-carboxylate (GARDNER and HAWORTH), T., 1958.
- $C_{14}H_{17}O_4N$ Methyl 1-phenylpyrrolidine-2:5-dicarboxylate (LE SUEUR), T., 277; P., 36.
- $C_{14}H_{17}O_6N$ 7-Mandelonitrile glucoside, isolation of, from *Prunus serotina* (POWER and MOORE), T., 243; P., 27.
Indican (+ 3H₂O), experiments on, and estimation of (PERKIN and THOMAS), T., 793; P., 125.
- $C_{14}H_{15}ON_2$ Cinnamenylpiperidylcarbamide (FORSTER), T., 439.
- $C_{14}H_{19}O_3N$ 1-Keto-6:7-dimethoxy-2-propyltetrahydroisoquinoline (PYMAN), T., 1748.
- $C_{14}H_{21}O_2N$ 6:7-Dimethoxy-2-propyltetrahydroisoquinoline, and its hydrochloride (PYMAN), T., 1748.
- $C_{14}H_{21}O_3N$ 4:5-Dimethoxy-2- β -propylaminoethylbenzaldehyde (PYMAN), T., 1747.
6:7-Dimethoxy-2-propyl-3:4-dihydroisoquinolinium hydroxide, chloride and picrate of (PYMAN), T., 1747.
- $C_{14}H_{21}O_6N$ Glucose-*p*-phenetidine (+ $\frac{1}{2}$ H₂O and + H₂O), properties of (IRVINE and GILMOUR), T., 1550; P., 219.
- $C_{14}H_{22}O_3N_4$ Tetraethylammonium styphnate, preparation and crystallography of (JERUSALEM), T., 1287.
- $C_{14}H_{23}O_4Br$ Ethyl α -bromo-1-methylcyclohexyl-4-malonate (HOPE and PERKIN), T., 1367.
- $C_{14}H_{25}ON$ *n*-Butyrobornylamide (FRANKLAND and BARROW), T., 2025; P., 263.

$C_{14}H_{26}O_4S_2$ Diethyl α -dithiodiisovalerate (PRICE and TWISS), T., 1055 ; P., 165.

14 IV

$C_{14}H_8O_3N_2S$ Ethyl 3-cyano-4-keto-2-phenyliminotetrahydrothiophen-3-carboxylate (RUHEMANN), T., 121.

$C_{14}H_9O_2N_4Br$ Dinitrohydroxy-1-*o*-, -*m*-, and -*p*-bromophenylmethylbenzimidazole (MELDOLA and HAY), T., 1040.

$C_{14}H_{10}O_2N_4S$ Dinitrohydroxy-1-*p*-sulphophenylmethylbenzimidazole (MELDOLA and HAY), T., 1047.

$C_{14}H_{10}O_9N_4S$ Dinitrohydroxy-1-*o*-hydroxyphenylmethylbenzimidazole-sulphonic acid (MELDOLA and HAY), T., 1044.

$C_{14}H_{11}O_3NS$ Benzenesulphonylmandelonitrile (FRANCIS and DAVIS), T., 1408.

$C_{14}H_{12}ONCl$ *o*-Methoxybenzylidene-*o*-chloroaniline (SENIER and SHEPHEARD), T., 1947.

$C_{14}H_{12}ONBr$ 5-Bromosalicylidene-*m*-toluidine (SENIER and SHEPHEARD), T., 1953.

$C_{14}H_{12}O_3N_2S$ *p*-Toluenesulphonyl derivative of 1-hydroxy-5-phenyltetrazole (FORSTER), T., 189 ; P., 25.

$C_{14}H_{12}O_4N_2S_2$ *o*-Nitrobenzyl disulphide, preparation of (PRICE and TWISS), T., 1490 ; P., 211.

$C_{14}H_{12}O_4N_2Se$ Nitrobenzyl diselenide (*o*-, *m*-, and *p*-) (PRICE and JONES), T., 1729 ; P., 234.

$C_{14}H_{14}ON_3Br$ Bromo-*o*-, -*m*-, and -*p*-tolylidiazohydroxylamino-*p*-toluene (GEBHARD and THOMPSON), T., 1119.

$C_{14}H_{12}O_9N_3Mo_2$ Benzoylmethyl-*p*-aminobenzenediazonium molybdate (MORGAN and ALCOCK), T., 1325 ; P., 202.

14 V

$C_{14}H_9ONCl_7P$ Substance, from phosphorus pentachloride and phenylbenzometoxazone, and benzoylsalicylonitrile (TITHERLEY and HICKS), T., 918.

$C_{14}H_{10}O_2NCl_4P$ Substance, from phosphorus pentachloride and phenylbenzometoxazone (TITHERLEY and HICKS), T., 919.

$C_{14}H_9O_2NCl_3P$ Substance, from phosphorus pentachloride and phenylbenzometoxazone, and benzoylsalicylonitrile (TITHERLEY and HICKS), T., 918.

$C_{14}H_{31}O_4I_3SHg$ Diacetaethylylsulphonium mercuri-iodide (CLARKE and SMILES), T., 1001.

 C_{15} Group.

$C_{15}H_8O_6$ Rhein, preparation of (ROBINSON and SIMONSEN), T., 1092.

$C_{15}H_{10}O_4$ Chrysophanic acid, constitution of (TUTIN and CLEWER), P., 200.

$C_{15}H_{10}O_5$ Emodin, constitution of (TUTIN and CLEWER), P., 200.

$C_{15}H_{10}O_7$ Quercetin, from *Thespesia lampas* (PERKIN), T., 1859 ; P., 248.

$C_{15}H_{10}O_8$ Gossypetin, from *Hibiscus sabdariffa* (PERKIN), T., 1855 ; P., 248.

$C_{15}H_{14}O_2$ 7-Benzoin methyl ether (WREN), T., 1584.

$C_{15}H_{14}O_7$ Carthamine (KAMETAKA and PERKIN), P., 223.

$C_{15}H_{26}O_3$ Ethyl α -benzoyl- α -ethylbutyrate, preparation of (HOPE and PERKIN), T., 2048.

$C_{15}H_{20}O_3$ Androsin (+ 2H₂O) (*acetovanillone glucoside*) (MOORE), T., 746 ; P., 85.

$C_{15}H_{26}O_5$ Ethyl α -methoxy-1-methylcyclohexyl-4-malonate (HOPE and PERKIN), T., 1368.

15 III

$C_{12}H_{10}O_3N_2$ *p*-Nitrobenzaldehydeindogenide, quantitative experiments with (PERKIN and THOMAS), T., 796 ; P., 125.

- $C_{15}H_{10}O_4N_2$ *m*-Nitrobenzoylmandelonitrile (FRANCIS and DAVIS), T., 1408.
- $C_{15}H_{10}O_7N_4$ Dinitrohydroxy-1-*o*-, -*m*-, and -*p*-carboxyphenylmethylbenzimidazole, and their silver salts (MELDOLA and HAY), T., 1041.
- $C_{15}H_{11}ON$ 2:5-Diphenyloxazole, synthesis of (ROBINSON), T., 2169; P., 295.
- $C_{15}H_{11}O_2N$ Benzoylmandelonitrile (FRANCIS and DAVIS), T., 1404.
- p -Hydroxybenzaldehydeindogenide (PERKIN and THOMAS), T., 799; P., 125.
- $C_{15}H_{11}O_3N$ Dihydroxybenzaldehydeindogenide (PERKIN and THOMAS), T., 798; P., 125.
- $C_{15}H_{12}OBr_2$ $\alpha\beta$ -Dibromobenzylacetophenone, stereoisomeric modifications of (SMEDLEY), P., 259.
- $C_{15}H_{13}ON$ *m*-Benzoylaminostyrene (+ H_2O), preparation of (TUTIN, CATON, and HANN), T., 2125.
- $C_{15}H_{13}O_2N$ Piperonylidene-*m*-toluidine (SENIER and SHEPHEARD), T., 1954.
- ω -Benzoylaminoacetophenone (ROBINSON), T., 2169; P., 295.
- $C_{15}H_{13}O_3N$ *o*-Methoxybenzylidene-*p*-aminobenzoic acid (SENIER and SHEPHEARD), T., 1949.
- $C_{15}H_{13}O_3N_3$ Benzoyl-*p*-aminobenzenediazonium acetate (MORGAN and ALCOCK), T., 1323; P., 202.
- $C_{15}H_{13}O_4N$ 5-Benzoyl amino-1-methoxy-2:3-methylenedioxybenzene (SALWAY), T., 1162.
- $C_{15}H_{14}ON_2$ Cinnamylphenylcarbamide (FORSTER), T., 439.
- $C_{15}H_{14}O_2N$ Benzoyl-*p*-hydroxyphenylethylamine (BARGER and WALPOLE), T., 1722; P., 229.
- $C_{15}H_{14}O_3N_2$ Benzoyl-*p*-nitrophenylethylamine (BARGER and WALPOLE), T., 1721; P., 229.
- $C_{15}H_{14}N_2S$ 3-Phenyl-6-methyl-2-thio-1:2:3:4-tetrahydroquinazoline, and its platinumchlorides (SENIER and SHEPHEARD), T., 499.
- $C_{15}H_{15}ON$ 2-Hydroxy-5-methylbenzylidene-*m*-toluidine (SENIER and SHEPHEARD), T., 1952.
- Anisylidene-*m*-toluidine, and its hydrochloride (SENIER and SHEPHEARD), T., 1952.
- Salicylidene-*o*-4-xylylidine (SENIER and SHEPHEARD), T., 1945.
- Salicylidene-*m*-4-xylylidine (SENIER and SHEPHEARD), T., 443.
- Salicylidene-*p*-xylylidine (SENIER and SHEPHEARD), T., 443.
- $C_{15}H_{15}ON_3$ Cinnamylphenylsemicarbazide (FORSTER), T., 439.
- $C_{15}H_{15}O_2N$ α -*p*-Hydroxy-*N*-benzoylphenylethylamine (TUTIN, CATON, and HANN), T., 2123.
- β -*p*-Hydroxy-*N*-benzoylphenylethylamine (BARGER), T., 1128.
- Vanillidene-*m*-toluidine (SENIER and SHEPHEARD), T., 1954.
- Salicyl-*m*- and -*p*-4-xylylidide (SENIER and SHEPHEARD), T., 444.
- $C_{15}H_{16}ON_2$ Benzoyl-*p*-aminophenylethylamine, and its hydrochloride (BARGER and WALPOLE), T., 1722; P., 229.
- as*-Benzoylethyl-*p*-phenylenediamine (MORGAN and ALCOCK), T., 1322; P., 202.
- $C_{15}H_{17}ON_3$ *p*-Methoxybenzenediazodimethylaniline, and absorption spectra of (HEWITT and THOMAS), T., 1298; P., 190.
- $C_{15}H_{19}O_2N$ Benzoyltropeine, and its salts (JOWETT and PYMAN), T., 1028.
- $C_{15}H_{19}O_3N$ *o*-, *m*-, and *p*-Hydroxybenzoyltropeine, and their salts (JOWETT and PYMAN), T., 1031.
- $C_{15}H_{20}O_2N_2$ Phenylcarbamotropeine, salts of (JOWETT and PYMAN), T., 1027.
- $C_{15}H_{21}O_5N$ Myristicinylideneaminoacetal, and its reduction products (SALWAY), T., 1211.

- $C_{15}H_{22}O_2N$ 5-Imino-2-cyano-1:3-dimethyl-6-ethyl-3-propyl- Δ^8 -cyclohexene-2-carboxylic acid (GARDNER and HAWORTH), T., 1962.
 $C_{15}H_{21}O_2N$ Myristicinylaminoacetal and its hydrochloride (SALWAY), T., 1212.
 $C_{15}H_{23}O_3Sb$ Amyl antimonite (MacKEY), T., 607; P., 98.
*iso*Amyl antimonite (MacKEY), T., 607; P., 98.

15 IV

- $C_{15}H_{10}O_2NCl$ *p*-Chlorobenzoylmandelonitrile (FRANCIS and DAVIS), T., 1406.
 $C_{15}H_{11}ON_2S_2$ Anhydrodiphenyldithiobiuretcarboxylic acid (RUEHMANN and PRIESTLEY), T., 455; P., 62.
 $C_{15}H_{17}O_4N_3Mo_2$ Benzylethyl-*p*-aminobenzenediazonium molybdate (MORGAN and ALCOCK), T., 1325; P., 202.
 $C_{15}H_{15}ON_3I$ *p*-Dimethylaminobenzenediazophenol methiodide (HEWITT and THOMAS), T., 1296; P., 190.

C₁₆ Group.

- $C_{16}H_{10}O_6$ Rhein methyl ester (ROBINSON and SIMONSEN), T., 1092; P., 76.
 $C_{16}H_{12}O_2$ Dibenzylethylene, refraction of (SMEDLEY), T., 219; P., 17.
 $C_{16}H_{12}O_3$ Benzoylbenzylideneacetic acid, and its sodium salt (RUEHMANN), T., 116.
 $C_{16}H_{12}O_4$ 2:3:6:7-Dimethylenetetraoxydihydroanthracene (EWINS), T., 1486; P., 211.
 $C_{16}H_{12}O_5$ Hydroxydimethoxyanthraquinone (ROBINSON and SIMONSEN), T., 1095.
 $C_{16}H_{12}O_6$ Chrysoeriol (TUTIN and CLEWER), T., 85; P., 12.
 $C_{16}H_{14}O_3$ *m*-Toluic anhydride (DENHAM), T., 1240.
 Acetyl-*l*-benzoin (WREN), T., 1585.
 $C_{16}H_{14}O_5$ Brazilin, derivatives of (PERKIN and ROBINSON), T., 381; P., 31.
 $C_{16}H_{14}O_6$ Hæmatoxylin, derivatives of (PERKIN and ROBINSON), T., 381; P., 31.
 $C_{16}H_{15}N$ Cinnamylidene-*m*-toluidine, and its hydrochloride (SENIER and SHEPHEARD), T., 1955.
 $C_{16}H_{18}O_4$ Pinacone, from *p*-hydroxyacetophenone (TUTIN, CATON, and HANN), T., 2122.
 $C_{16}H_{19}N$ Aminotetramethyldiphenyl (CROSSLEY and HAMPSHIRE), P., 163.
 $C_{16}H_{20}N_2$ Diphenyldimethylethylenediamine, dihydrochloride of (DUNLOP and JONES), T., 418.
 $C_{16}H_{24}O_6$ Diethyl 6-acetyl-1:5-dimethylcyclohexan-3-one-2:6-dicarboxylate (RUEHMANN), T., 115.
 $C_{16}H_{28}O_5$ Ethyl α -ethoxycyclohexylmalonate (HOPE and PERKIN), T., 1366.
 $C_{16}H_{29}Si$ Benzylethylpropylisobutylsilicane (KIPPING and DAVIS), T., 73; P., 9.

16 III

- $C_{16}H_9ON$ Phenyliminocamphor (FORSTER and THORNLEY), T., 949.
 $C_{16}H_9O_{10}N$ Nitrodiphenyltetra-carboxylic acid (CROSSLEY and HAMPSHIRE), P., 162.
 $C_{16}H_{10}O_2N_2$ Indirubin, reduction of (PERKIN), P., 127.
 $C_{16}H_{10}O_2Cl_2$ 5:8-Dichloro-1:2-, -1:3-, and -1:4-dimethylantraquinone (HARROP, NORRIS, and WEIZMANN), T., 1314.
 $C_{16}H_{11}O_7N_4$ 2:5-Dinitroresorcinolazo- β -naphthol (MELDOLA and HAY), T., 1385.

- $C_{16}H_{13}O_2N$ Diketodiphenylpyrroline (RUHEMANN), T., 989.
- $C_{16}H_{11}O_3N$ Methyleneedioxybenzaldehydeindogenide (PERKIN and THOMAS), T., 796; P., 125.
- $C_{16}H_{11}O_3N_3$ 4-Nitro-2-benzeneazo- α -naphthol (MITCHELL and SMITH), T., 1434; P., 209.
2-Nitro-4-benzeneazo- α -naphthol (MITCHELL and SMITH), T., 1432; P., 209.
- $C_{16}H_{11}O_4N$ Benzoyloxyhomopiperonylonitrile (FRANCIS and DAVIS), T., 1406.
- $C_{16}H_{12}O_2N_2$ Phenylpropionylphenylcarbamide (RUHEMANN), T., 1609; P., 220.
Oxime of diketodiphenylpyrroline (RUHEMANN), T., 1605.
- $C_{16}H_{12}O_2N_4$ Tetraketo-2:5-dianilinopiperazine (DE MOULPIED and RULE), T., 551.
- $C_{16}H_{12}O_3Cl_2$ 3:6-Dichloro-2':3', -2':4', and -2':5'-dimethyl-2-benzoylbenzoic acid (HARROR, NORRIS, and WEIZMANN), T., 1314.
- $C_{16}H_{12}O_5N_2$ *m*-Nitrobenzoyl-*p*-methoxymandelonitrile (FRANCIS and DAVIS), T., 1408.
- $C_{16}H_{13}ON$ 5-Phenyl-2-benzylloxazole, and picrate of (ROBINSON), T., 2170; P., 295.
- $C_{16}H_{13}O_2N$ Benzoyl-*p*-tolylglycollonitrile (FRANCIS and DAVIS), T., 1405.
Diketodiphenylpyrrolidine (RUHEMANN), T., 990.
- $C_{16}H_{13}O_3N$ *p*-Anisoylmandelonitrile (FRANCIS and DAVIS), T., 1407.
Benzoyl-*o*- and -*p*-methoxymandelonitrile (FRANCIS and DAVIS), T., 1405.
- $C_{16}H_{13}O_4N$ Aminodimethoxyanthraquinone (ROBINSON and SIMONSEN), T., 1095.
- $C_{16}H_{14}O_3N$ Substance, from anisaldehydecyanohydrin and hydrogen chloride (McCOMBIE and PARRY), T., 587; P., 95.
- $C_{16}H_{14}O_4S_2$ Substance, from sulphur monochloride and silver phenylacetate (DENHAM), T., 1239.
Substance, from sulphur monochloride and silver *o*-toluate (DENHAM), T., 1239.
Substance, from sulphur monochloride and silver *m*-toluate (DENHAM), T., 1239.
Substance, from sulphur monochloride and silver *p*-toluate (DENHAM), T., 1240.
- $C_{16}H_{15}O_3N$ ω -Phenylacetylaminacetophenone (ROBINSON), T., 2170; P., 295.
- $C_{16}H_{15}O_4N$ 1:2-Dihydropapaveroline, and its hydrochloride (+ $\frac{1}{2}H_2O$) (PYMAN), T., 1622.
- $C_{16}H_{16}O_2N_2$ ω -Phenylacetylaminacetophenoneoxime (ROBINSON), T., 2170; P., 295.
4-Nitroso-4'-acetylamin-3:3'-ditolyl (CAM), T., 717; P., 123.
- $C_{16}H_{16}N_2S$ 3-*o*- and -*p*-Tolyl-6-methyl-2-thio-1:2:3:4-tetrahydroquinazoline (SENIER and SHEPHEARD), T., 503.
- $C_{16}H_{16}N_4Si$ Silicotetrapyrrole (REYNOLDS), T., 505.
- $C_{10}H_{17}ON$ *o*-Methoxybenzylidene-*o*-4-xylylidine (SENIER and SHEPHEARD), T., 1946.
Salicylidene- ψ -cumidine (SENIER and SHEPHEARD), T., 443.
- $C_{16}H_{17}O_3N$ α -Hydroxy- β -phenylacetylamin- α -phenylethane (ROBINSON), T., 2171; P., 295.
Salicyl- ψ -cumidide (SENIER and SHEPHEARD), T., 444.
Nitrotetramethyldiphenyl (CROSSLEY and HAMPSHIRE), P., 162.
- $C_{16}H_{17}O_2N_3$ *p*-Dimethylaminobenzeneazophenyl acetate (HEWITT and THOMAS), T., 1296; P., 190.
- $C_{16}H_{17}O_3N_3$ *o*-, *m*-, and -*p*-Carbomethoxybenzenediazohydroxylamino-*p*-toluene (GEBHARD and THOMPSON), T., 773.

- $C_{16}H_{17}O_4N$ Tetrahydropapaveroline, hydrochloride of (PYMAN), T., 1619.
- $C_{16}H_{18}ON_2$ Acetylolidine (+H₂O) (CAIN), T., 717; P., 123.
- $C_{16}H_{19}O_2N$ *m*- and *p*-Hydroxyphenyliminocamphor (FORSTER and THORNLEY), T., 950, 954.
- $C_{16}H_{19}O_5N$ Glucose- β -naphthylamide (+H₂O) (IRVINE and GILMOUR), T., 1552; P., 219.
- $C_{16}H_{20}O_2N_2$ Nitrosophenylaminocamphor (FORSTER and THORNLEY), T., 950.
- $C_{16}H_{20}O_3N_4$ Camphoryl-*o*-, *m*-, and *p*-nitrophenyltriazen (FORSTER and GARLAND), T., 2062.
- $C_{16}H_{21}ON$ Phenylaminocamphor (FORSTER and THORNLEY), T., 950.
- $C_{16}H_{21}ON_3$ Phenylhydrazone of isonitrosocamphor, isomeric forms of (FORSTER and THORNLEY), T., 956.
- Oxime of camphorquinonephenylhydrazone (FORSTER and THORNLEY), T., 955.
- Camphorylphenyltriazen, and its silver derivative (FORSTER and GARLAND), T., 2051; P., 244.
- $C_{16}H_{21}O_2N$ *p*-Hydroxyphenylaminocamphor (FORSTER and THORNLEY), T., 951.
- Phenylacetiltropeine, salts of (JOWETT and PYMAN), T., 1028.
- $C_{16}H_{21}O_4N$ Ethyl 1-phenylpyrrolidine-2:5-dicarboxylate (LE SUEUR), T., 276; P., 36.
- $C_{16}H_{22}O_2N_2$ Phenylaminoacetyl tropeine, and its dihydrobromide and dipicrate (JOWETT and PYMAN), T., 1025.
- $C_{16}H_{22}O_3N_2$ α -Hydroxy- β -2-pyridylpropionyl tropeine, and its salts (JOWETT and PYMAN), T., 1024.

16 IV

- $C_{16}H_8O_3N_3Br_3$ 2':4':6'-Tribromo-4-nitro-2-benzeneazo- α -naphthol (MITCHELL and SMITH), T., 1436; P., 209.
- 2':4':6'-Tribromo-2-nitro-4-benzeneazo- α -naphthol (MITCHELL and SMITH), T., 1436; P., 209.
- $C_{16}H_8O_6N_2Cl_2$ 5:8-Dichlorodinitro-1:2-dimethylantraquinone (HARROP, NORRIS, and WEIZMANN), T., 1315.
- $C_{16}H_8O_4NCl_2$ 5:8-Dichloronitro-1:3- and -1:4-dimethylantraquinone (HARROP, NORRIS, and WEIZMANN), T., 1317.
- $C_{16}H_{11}ONBr_2$ Dibromodiketodiphenylpyrrolidine (RUHEMANN), T., 1605.
- $C_{16}H_{11}O_2NS$ 2:4-Diketo-3-phenyl-5-benzylidenetetrahydrothiazole (RUHEMANN), T., 120.
- $C_{16}H_{11}O_2NS$ 2:4-Diketo-3-phenyl-5-salicylidenetetrahydrothiazole (RUHEMANN), T., 120.
- $C_{16}H_{11}O_3N_3S$ 1:3-Diphenyl-2-thiovioluric acid (ISHERWOOD), P., 121; (WHITELEY and MOUNTAIN), P., 122.
- $C_{16}H_{11}O_3Cl_2Br$ 3:6-Dichloro-5'-bromo-2':4'-dimethyl-2-benzoylbenzoic acid, and its sodium salt (HARROP, NORRIS, and WEIZMANN), T., 1316.
- $C_{16}H_{12}O_3N_2S$ 1:3-Diphenylthiobarbituric acid, preparation of (ISHERWOOD), P., 121; (WHITELEY and MOUNTAIN), P., 121.
- $C_{16}H_{14}O_2N_2Cl_2$ 3:3'-Dichloro-4:4'-diacetyldiaminoazobenzene (CAIN), T., 716; P., 123.
- $C_{16}H_{16}O_3N_2Br$ Bromo-*o*-carbethoxybenzenediazohydroxylamino-*p*-toluene (GEBHARD and THOMPSON), T., 1121.
- $C_{16}H_{17}O_2NS$ Diethyl 4-keto-2-phenyliminotetrahydrothiophen-3-dicarboxylate (RUHEMANN), T., 121.
- $C_{17}H_{25}ONCl$ *p*-Chlorophenyliminocamphor (FORSTER and THORNLEY), T., 954.

- $C_{16}H_{20}ONCl$ *p*-Chlorophenylaminocamphor (FORSTER and THORNLEY), T., 954.
- $C_{16}H_{20}ON_3Br$ Camphoryl-*p*-bromophenyltriazen (FORSTER and GARLAND), T., 2065.
- $C_{16}H_{20}ON_3I$ *p*-Methoxybenzeneazodimethylaniline methiodide (HEWITT and THOMAS), T., 1298; P., 190.
- $C_{16}H_{20}O_2NCl$ Phenylechloroacetyl tropeine, and its salts (JOWETT and PYMAN), T., 1024.
- $C_{16}H_{20}O_3NS$ *l*-Menthylamine benzenesulphonate (KIPPING and MARTIN), T., 493; P., 66.
- $C_{16}H_{28}O_3SSi$ *dl*-Benzylethylpropylisobutylsilicanesulphonic acid, and its salts (KIPPING and DAVIS), T., 69; P., 9.

16 V

- $C_{16}H_{16}O_5NBr_2S$ Diethyl-5-dibromo-4-keto-2-phenyliminotetrahydrothiophen-3-dicarboxylate (RUHEMANN), T., 122.

C₁₇ Group.

- $C_{17}H_{12}O_6$ Dimethylrhein (ROBINSON and SIMONSEN), T., 1093; P., 76.
Rhein ethyl ester (ROBINSON and SIMONSEN), T., 1092; P., 76.
- $C_{17}H_{14}O_4$ Chrysophanic acid dimethyl ether (TUTIN and CLEWER), P., 302.
- $C_{17}H_{17}N$ 2:3:7:8-Tetramethylacridine, and its aurichloride and platinichloride (SENIER and COMPTON), T., 1626; P., 220.
- $C_{17}H_{20}O_5$ *o*-Aldehydophenyl hydrogen camphorate, and its rotatory power (HILDITCH), T., 337.
- $C_{17}H_{22}O_4$ *o*-Tolyl hydrogen camphorate, and its rotatory power (HILDITCH), T., 337.
- $C_{17}H_{28}O_8$ Ethyl pentane- $\alpha\delta\epsilon$ -tetracarboxylate (DOBSON, FERNS, and PERKIN), T., 2011; P., 263.
- $C_{17}H_{28}O_9$ Ethyl δ -methoxybutane- $\alpha\alpha\gamma\gamma$ -tetracarboxylate (PERKIN and SIMONSEN), T., 1171.

17 III

- $C_{17}H_{11}O_4N$ 2:3-Diketo-4-phenyl-5-piperonylpyrroline (RUHEMANN), T., 1608.
- $C_{17}H_{11}O_4Cl$ Dimethylrhein chloride (ROBINSON and SIMONSEN), T., 1094; P., 76.
- $C_{17}H_{13}ON$ Salicylidene- α -naphthylamine (SENIER and SHEPHEARD), T., 443.
- $C_{17}H_{13}O_2N$ Phenylpropionylphenylacetamide (RUHEMANN), T., 991.
Cinnamoylmandelonitrile (FRANCIS and DAVIS), T., 1408.
 α -Benzoyloxy- γ -phenylisocrotononitrile (FRANCIS and DAVIS), T., 1406.
Salicyl- α - and - β -naphthalide (SENIER and SHEPHEARD), T., 444, 445.
2:3-Diketo-4-phenyl-5-*o*-tolylpyrroline (RUHEMANN), T., 990.
2:3-Diketo-4-phenyl-5-*m*- and -*p*-tolylpyrroline (RUHEMANN), T., 1606.
- $C_{17}H_{13}O_3N$ 2:3-Diketo-4-phenyl-5-anisylpyrroline (RUHEMANN), T., 1607.
p-Acetoxybenzaldehydeindogenide (PERKIN and THOMAS), T., 799; P., 125.
- $C_{17}H_{15}O_5N$ Dimethylrheinamide (ROBINSON and SIMONSEN), T., 1095; P., 76.
- $C_{17}H_{15}O_2N_2$ Phenylpropionyl-*p*-tolylcarbamide (RUHEMANN), T., 1609; P., 220.

- $C_{17}H_{14}O_2N$ Dinitrohydroxy-1-*o*-, -*m*-, and -*p*-carbethoxyphenylmethylbenzimidazole (MELDOLA and HAY), T., 1041, 1042.
- $C_{17}H_{15}O_3N$ 2-Phenyl-5-veratryloxazole, and its hydrochloride (ROBINSON), T., 2172; P., 295.
- $C_{17}H_{15}O_4N$ *p*-Anisoyl-*p*-methoxymandelonitrile (FRANCIS and DAVIS), T., 1407.
- $C_{17}H_{16}O_3N_4$ Dinitrohydroxy-1-(1:3:5)-trimethylphenylmethylbenzimidazole (MELDOLA and HAY), T., 1047.
- $C_{17}H_{19}O_3N$ Benzoyl- β -amino- β' -*o*-tolylxyisopropyl alcohol (BOYD and KNOWLTON), T., 1805.
- $C_{17}H_{20}O_3N_2$ *o*-, *m*-, and *p*-Nitroanilino-*d*-methylenecamphor (POPE and READ), T., 182.
- $C_{17}H_{20}O_3S$ *o*-Aldehydophenyl camphor- β -sulphonate, and its rotatory power (HILDITCH), T., 338.
- $C_{17}H_{21}ON$ Anilino-*d*-methylenecamphor, rotatory power of (POPE and READ), T., 177; P., 19.
- $C_{17}H_{21}O_2N$ *p*-Methoxyphenyliminocamphor (FORSTER and THORNLEY), T., 952.
- Cinnamoyltropeine, and its salts (JOWETT and PYMAN), T., 1029.
- $C_{17}H_{21}N_2I$ Methiodide of diphenylpiperazine (DUNLOP and JONES), T., 419.
- $C_{17}H_{22}O_2N_2$ Camphorylphenyl- ψ -carbamide (FORSTER and GARLAND), T., 2061.
- $C_{17}H_{22}O_3N_2$ *o*-, *m*-, and *p*-Nitrobenzobornylamide (FRANKLAND and BARROW), T., 2035; P., 263.
- $C_{17}H_{22}O_3N_4$ Camphoryl-*o*-, -*m*-, and -*p*-nitrophenylmethyltriazene (FORSTER and GARLAND), T., 2067.
- $C_{17}H_{22}O_4S$ *o*-Tolyl camphor- β -sulphonate, and its rotatory power (HILDITCH), T., 338.
- $C_{17}H_{23}ON_3$ Camphorylphenylmethyltriazene (FORSTER and GARLAND), T., 2066.
- $C_{17}H_{23}O_2N$ *p*-Methoxyphenylaminocamphor (FORSTER and THORNLEY), T., 952.
- $C_{17}H_{23}O_2N_3$ Camphoryl-*p*-methoxyphenyltriazene (FORSTER and GARLAND), T., 2064.
- $C_{17}H_{23}O_3N$ α -Hydroxy- β -phenylpropionyltropeine, and its salts (JOWETT and PYMAN), T., 1023.
- Atropine, resolution of, and its aurichloride, auribromide and picrate (BARROWCLIFF, and TUTIN), T., 1966; P., 256.
- d*-Hyoscyamine, auribromide (+H₂O) and picrate (BARROWCLIFF and TUTIN), T., 1976; P., 257.
- $C_{17}H_{23}O_4N$ Atroglyceryltropeine, and its salts (JOWETT and PYMAN), T., 1022.
- $C_{17}H_{23}N_2I$ Methiodide of diphenyldimethylethylenediamine (DUNLOP and JONES), T., 418.

17 IV

- $C_{17}H_{12}O_3N_4S$ β -Naphthalenesulphonyl derivative of 1-hydroxy-5-phenyltetrazole (FORSTER), T., 189; P., 25.
- $C_{17}H_{13}ON_2Br$ Bromo-*o*- and -*m*-tolueneazo- β -naphthol (GEBHARD and THOMPSON), T., 1120.
- $C_{17}H_{22}ON_3Br$ Camphoryl-*p*-bromophenylmethyltriazene, and its salts (FORSTER and GARLAND), T., 2070.
- $C_{17}H_{23}O_3NS$ Camphor- β -sulphonyl-*p*-toluidide, and its rotatory power (HILDITCH), T., 338.

17 V

$C_{17}H_{23}O_2NClBr$ Methobromide of phenylchloroacetyltryptone (JOWETT and PYMAN), T., 1024.

 C_{18} Group.

$C_{18}H_{10}O_2$ Naphthacenequinone, derivatives of (HARROP, NORRIS, and WEIZMANN), T., 279; P., 33.

$C_{18}H_{14}O_5$ Trimethoxycoumaronoisocoumarin, and its hydrobromide (PERKIN and ROBINSON), T., 401.

$C_{18}H_{14}O_7$ Xanthoeridol (TUTIN and CLEWER), T., 84; P., 12.

$C_{18}H_{15}N$ γ -Cyano- $\beta\epsilon$ -diphenyl- Δ^{85} -pentadiene (HAWORTH), T., 487.

$C_{18}H_{16}O_7$ Lactone of hydroxytrimethoxybenzoinearboxylic acid (PERKIN and ROBINSON), T., 405.

$C_{18}H_{18}O_3$ α -Desylisobutyric acid, formation of (GRAY), T., 2148.

$C_{18}H_{18}O_8$ Hydroxytrimethoxybenzoinearboxylic acid (PERKIN and ROBINSON), T., 404.

$C_{18}H_{18}N_2$ β -Imino- α -cyano- $\alpha\gamma$ -di-*o*-, *m*-, and *p*-tolylpropane (BEST and THORPE), T., 265; P., 28.

6-*o*-Tolyl-1-methyl-5:7-naphthylenediamine, and its dihydrochloride (BEST and THORPE), T., 266; P., 29.

6-*m*-Tolyl-2-methyl-5:7-naphthylenediamine, and its dihydrochloride (BEST and THORPE), T., 269; P., 29.

7-*p*-Tolyl-2-methyl-6:8-naphthylenediamine, and its dihydrochloride (BEST and THORPE), T., 272; P., 29.

$C_{18}H_{18}N_8$ Bisbenzeneazophenylenediamine (*Bismarck-brown*), rate of formation of (VELEY), T., 1189; P., 175.

$C_{18}H_{20}O_4$ Substance, from oxidation of laudanose (PYMAN), T., 1269.

$C_{18}H_{26}O_3$ Menthyl *r*-mandelate, partial racemisation of, and the *B*/*A*- and *B*/*B*/*A*-salts and their solubilities (FINDLAY and HICKMANS), T., 1386; P., 196.

18 III

$C_{18}H_6O_3Cl_4$ 7:8:9:10-Tetrachloro-1-hydroxynaphthacenequinone (HARROP, NORRIS, and WEIZMANN), T., 287.

$C_{18}H_6O_4Cl_4$ 7:8:9:10-Tetrachloro-1:6-dihydroxynaphthacenequinone (HARROP, NORRIS, and WEIZMANN), T., 287.

$C_{18}H_8O_3Cl_2$ 7:10-Dichloro-1-hydroxynaphthacenequinone (HARROP, NORRIS, and WEIZMANN), T., 283.

$C_{18}H_8O_4Cl_2$ 7:10-Dichloro-1:5- and -1:6-dihydroxynaphthacenequinone (HARROP, NORRIS, and WEIZMANN), T., 283, 284.

$C_{18}H_8O_4Cl_4$ 3:4:5:6-Tetrachloro-1'-hydroxy-2- β -naphthoylbenzoic acid, and its sodium salt (HARROP, NORRIS, and WEIZMANN), T., 286.

$C_{18}H_{10}O_4Cl_2$ 3:6-Dichloro-1'-hydroxy-2- β -naphthoylbenzoic acid (HARROP, NORRIS, and WEIZMANN), T., 282.

$C_{18}H_{12}O_2N_2$ Hydroxyaposafrone, preparation of (HEWITT, NEWMAN, and WINMILL), T., 581; P., 86.

$C_{18}H_{12}O_6As_2$ Resorcinyll arsenite (LANG and WOODHOUSE), P., 199.

$C_{18}H_{13}O_4N_3$ 4-Nitro-2-benzeneazo- α -naphthyl acetate (MITCHELL and SMITH), T., 1435; P., 209.

2-Nitro-4-benzeneazo- α -naphthyl acetate (MITCHELL and SMITH), T., 1433; P., 209.

$C_{18}H_{13}O_5N$ *p*-Acetoxy- ω -phthaliminoacetophenone (TUTIN, CATON, and HANN), T., 2119.

$C_{18}H_{15}O_6Br$ Bromotrimethoxycoumaronoisocoumarin (PERKIN and ROBINSON), T., 403.

- $C_{18}H_{14}ON_2$ Methylenephényl- α -naphthylcarbamide (SENIER and SHEPHEARD), T., 504.
- $C_{18}H_{13}ON_4$ Benzeneazobenzeneazophenol, dihydrochloride (HEWITT and THOLE), T., 1396; P., 208.
- $C_{18}H_{14}O_2N_4$ Dinitroacetoxy-1-*o*-, -*m*-, and -*p*-acetoxyphenylmethylbenzimidazole (MELDOLA and HAY), T., 1044, 1046.
- $C_{18}H_{15}ON$ 2-Hydroxy- α -naphthylidene-*m*-toluidine (SENIER and SHEPHEARD), T., 1954.
- $C_{18}H_{17}O_3N$ Cinnamoyl-*p*-methoxymandelonitrile (FRANCIS and DAVIS), T., 1408.
- $C_{18}H_{17}O_3Sb$ Phenyl antimonite (MACKEY), T., 608; P., 98.
- $C_{18}H_{15}O_7N$ Substance, from chloroxylonine and hydriodic acid (AULD), T., 967.
- $C_{18}H_{16}ON_2$ *s-p*-Tolyl- α -naphthylcarbamide (SENIER and SHEPHEARD), T., 502.
- $C_{18}H_{16}ON_4$ Phenosafranine, constitution of (HEWITT, NEWMAN, and WINMILL), T., 577; P., 86.
- $C_{18}H_{16}O_3N_2$ 3-Keto-2:5-di-*p*-methoxydiphenyl-3:4-dihydro-1:4-diazine, and its hydrochloride and picrate (McCOMBIE and PARRY), T., 588; P., 95.
- $C_{18}H_{16}O_5N_4$ Substance, from phenylhydrazine and oxidation products of mucic acid (FERRABOSCHI), T., 1249.
- $C_{18}H_{16}OSi$ Triphenylsilicic acid, action of fuming sulphuric acid on (KIPPING and MARTIN), T., 489; P., 66.
- $C_{18}H_{17}ON$ γ -Cyano- ϵ -hydroxy- $\beta\epsilon$ -diphenyl- $\Delta\beta$ -pentene (HAWORTH), T., 488.
- $C_{18}H_{17}O_2N$ Benzoylbenzylglycollonitrile (FRANCIS and DAVIS), T., 1406.
- $C_{18}H_{17}O_3N$ 2-Benzyl-5-veratryloxazole (ROBINSON), T., 2173; P., 295.
- $C_{18}H_{17}O_4N$ 2-Benzoylamino-5:6-dimethoxy-1-hydrindone (ROBINSON), T., 2173; P., 296.
- $C_{18}H_{18}O_3N_2$ Monoanilide of 1-phenylpyrrolidine-2:5-dicarboxylic acid (LE SUEUR), T., 278.
- $C_{18}H_{19}O_4N$ ω -Phenylacetylaminoveratrone (ROBINSON), T., 2172; P., 296.
- $C_{18}H_{20}ON$ Methylanilino-*d*-methylenecamphor, rotatory power of (POPE and READ), T., 179.
p-Toluidino-*d*-methylenecamphor, rotatory power of (POPE and READ), T., 177; P., 19.
- $C_{18}H_{21}O_2N$ *p*-Ethoxyphenyliminocamphor, and its hydrochloride (FORSTER and THORNLEY), T., 952.
- $C_{18}H_{23}ON$ *o*-, *m*-, and *p*-Toluobornylamide (FRANKLAND and BARROW), T., 2040; P., 263.
- $C_{18}H_{23}O_2N_3$ Camphoryl-*p*-methoxyphenylmethylnitriazene (FORSTER and GARLAND), T., 2069.
- $C_{18}H_{25}O_7N$ Senecifolidine, and its salts (WATT), T., 475; P., 68.
- $C_{18}H_{26}O_3N_2$ Hydroxylamino-derivative of *p*-ethoxyphenyliminocamphor (FORSTER and THORNLEY), T., 952.
- $C_{18}H_{26}N_4I_2$ Dimethiodide of diphenyldimethylethylenediamine (DUNLOP and JONES), T., 418.
- $C_{18}H_{27}O_5N$ Senecifoline, and its salts (WATT), T., 469; P., 68.

18 IV

- $C_{18}H_7O_4Cl_4Br$ 3:4:5:6-Tetrachloro-4'-bromo-1'-hydroxy-2- β -naphthoylbenzoic acid, and its sodium salt (HARROP, NORRIS, and WEIZMANN), T., 287.
- $C_{18}H_9O_3NCl_2$ 7:10-Dichloro-6-amino-1-hydroxynaphthacenequinone (HARROP, NORRIS, and WEIZMANN), T., 284.

- $C_{18}H_9O_4Cl_2Br$ 3:6-Dichloro-4'-bromo-1'-hydroxy-2- β -naphthoylbenzoic acid (HARROP, NORRIS, and WEIZMANN), T., 283.
- $C_{18}H_{13}O_2NS$ 2:4-Diketeto-3-phenyl-5-cinnamylidene tetrahydrothiazole (RÜHEMANN), T., 120.
- $C_{18}H_{15}O_5N_3Hg$ 4-Nitro-2-benzeneazo- α -naphthol mercuriacetate (MITCHELL and SMITH), T., 1435; P., 209.
2-Nitro-4-benzeneazo- α -naphthol mercuriacetate (MITCHELL and SMITH), T., 1433; P., 209.
- $C_{18}H_{14}O_3N_2Hg$ β -Benzeneazo- α -naphthol mercuriacetate (MITCHELL and SMITH), T., 1434; P., 209.
- $C_{18}H_{16}O_4NSb$ Triphenylstibine hydroxynitrate (MORGAN, MICKLETHWAIT, and WHITBY), P., 302.
- $C_{18}H_{18}ON_3As$ Triaminotriphenylarsine oxide, and its hydrochloride and platinichloride (MORGAN and MICKLETHWAIT), T., 1474; P., 212.
- $C_{18}H_{22}O_2NI$ Benzoylthordenine methiodide (BARGER), T., 2197.
- $C_{18}H_{23}O_4NS$ Camphor- β -sulphonyl-*p*-acetylanilide, and its rotatory power (HILDITCH), T., 339.
- $C_{18}H_{24}O_2NBr$ Methobromide of cinnamoyltropeine (JOWETT and PYMAN), T., 1030.
- $C_{18}H_{25}O_3NS$ Camphor- β -sulphonyl-*p*-ethylphenylamide, and rotatory power of (HILDITCH), T., 339.
- $C_{18}H_{26}O_3NBr$ Methobromide of α -hydroxy- β -phenylpropionyltropeine (JOWETT and PYMAN), T., 1023.
- $C_{18}H_{26}O_4NBr$ Methobromide of atroglyceryltropeine (JOWETT and PYMAN), T., 1022.
- $C_{18}H_{26}O_5NS$ Tropinone *d*-camphorsulphonate (+ H_2O) (BARROWCLIFF and TUTIN), T., 1973.
- $C_{18}H_{26}O_5NS$ Tropine *d*-camphorsulphonate (BARROWCLIFF and TUTIN), T., 1970; P., 257.
 ψ -Tropine *d*-camphorsulphonate (BARROWCLIFF and TUTIN), T., 1971; P., 257.

18 V

- $C_{18}H_{30}O_5NBrS$ ψ -Tropine *d*-bromocamphorsulphonate (+ H_2O) (BARROWCLIFF and TUTIN), T., 1971; P., 257.

C_{19} Group.

- 6-N-6
 $C_{19}H_{11}N_3$ $\begin{matrix} | \\ \text{---} \\ | \end{matrix}$ -Diquinacridine, and its salts (SENIER and COMPTON), T., 1629; P., 220.
5-CH-5
- $C_{19}H_{12}O_8$ Diacetylrhein, preparation of (ROBINSON and SIMONSEN), T., 1090; P., 76.
- $C_{19}H_{14}O_6$ 7-Methoxy-5:6-methylenedioxy-2-piperonylidene-1-hydrindone (PERKIN, ROBINSON, and THOMAS), T., 1983.
Trimethoxy- α - and - β -brazanquinone (PERKIN and ROBINSON), T., 394, 398.
- $C_{19}H_{15}N$ $\begin{matrix} N-\alpha & N-\beta \\ | & | \\ \text{---} & \text{---} \\ CH-\beta & CH-\alpha \end{matrix}$ - and - -naphthacridine, and their salts (SENIER and COMPTON), T., 1627, 1628; P., 220.
- $C_{19}H_{16}O_5$ α - and - β -Anhydrotrimethylbrazilone, constitution of (PERKIN and ROBINSON), T., 381; P., 31.
- $C_{19}H_{16}O_6$ Dimethylrhein ethyl ester (ROBINSON and SIMONSEN), T., 1093; P., 76.
- $C_{19}H_{16}O_7$ Tetramethoxycoumaronoisocoumarin, hydrobromide of (PERKIN and ROBINSON), T., 407.

- $C_{19}H_{18}O_2$ Anhydroacetonebenzil, direct proofs of the presence of the hydroxyl group in derivatives of (GRAY), T., 2131; P., 218; isomerides of, and its derivatives (GRAY), T., 2138; P., 218.
- 4-Methoxy-3:4-diphenyl-2-methyl- Δ^2 -cyclopentenone (GRAY), T., 2135.
- 3:4-Diphenyl-5:5-dimethyl- Δ^2 -cyclopenten-1-one-2-ol (GRAY), T., 2146.
- $C_{19}H_{18}O_4$ $\beta\gamma$ -Diphenyl- $\alpha\alpha$ -dimethylbutyrolactone- γ -carboxylic acid (+ H_2O), and its silver salt (GRAY), T., 2148.
- $C_{19}H_{18}O_6$ Trimethylbrazilone, constitution of (PERKIN and ROBINSON), T., 381; P., 31.
- $C_{19}H_{18}O_7$ Lactone of tetramethoxybenzoiccarboxylic acid (PERKIN and ROBINSON), T., 405.
- Eriodonol, (and + H_2O) (TUTIN and CLEWER), T., 86; P., 12.
- $C_{19}H_{20}O$ 3:4-Diphenyl-5:5-dimethylcyclopentenone (GRAY), T., 2147.
- $C_{19}H_{20}O_3$ Ethyl α -benzoyl- β -phenylisobutyrate (HOPE and PERKIN), T., 2046.
- $C_{19}H_{20}O_5$ α -Hydroxy- $\alpha\beta$ -diphenyl- $\gamma\gamma$ -dimethylglutaric acid, sodium salt (GRAY), T., 2150.

19 III

- $C_{19}H_{13}O_2N$ Benzoyl- β -naphthylglycollonitrile (FRANCIS and DAVIS), T., 1406.
- $C_{19}H_{15}O_2N$ Lactone of γ -cyano- ϵ -hydroxy- $\beta\epsilon$ -diphenyl- $\Delta\alpha$ -pentene- γ -carboxylic acid (HAWORTH), T., 487.
- $C_{19}H_{15}O_5N$ Diacetoxybenzaldehydeindogenide (PERKIN and THOMAS), T., 798; P., 125.
- $C_{19}H_{15}O_7N$ Nitro- α -anhydrotrimethylbrazilone (PERKIN and ROBINSON), T., 393.
- $C_{19}H_{16}O_3N_2$ *m*-Carbethoxybenzeneazo- β -naphthol (GEBHARD and THOMPSON), T., 1121.
- $C_{19}H_{17}O_2N$ 2:3-Diketo-4-phenyl-5-cumylpyrroline (RUHEMANN), T., 1607.
- $C_{19}H_{17}O_5N$ γ -Cyano- ϵ -hydroxy- $\beta\epsilon$ -diphenyl- $\Delta\alpha$ -pentene- γ -carboxylic acid (HAWORTH), T., 487.
- $C_{19}H_{18}ON_2$ Diaminotriphenylcarbinol, rate of reaction of, with acid and alkali (SIDGWICK and RIVETT), T., 899; P., 124.
- $C_{19}H_{19}O_2N$ Oxime of $\beta\beta$ -dimethylanhydroacetonebenzil (GRAY), T., 2147.
- $C_{19}H_{21}ON$ Oxime of 3:4-diphenyl-5:5-dimethylcyclopentenone (GRAY), T., 2148.
- $C_{19}H_{21}O_2N$ Benzoyl derivative of 3-cyano-1:2:4-trimethyl-4-ethyl- $\Delta^{1:5}$ -cyclohexadien-6-ol (GARDNER and HAWORTH), T., 1960.
- $C_{19}H_{24}O_4N_4$ Methylglucosazone (IRVINE and HYND), T., 1225.
- $C_{19}H_{25}ON$ *d*- and *l*- α -Phenylethylamino-*d*-methyleneamphor (POPE and READ), T., 172, 174.

19 IV

- $C_{19}H_{16}ON_3P$ Phenyliminophosphorylphenylbenzamidine (TITHERLEY and WORRALL), T., 1154; P., 150.
- $C_{19}H_{16}O_2N_2S$ 1:3-Diphenyl-5-isopropenyl-2-thiobarbituric acid (WHITELEY and MOUNTAIN), P., 121.
- $C_{19}H_{15}O_2N_2S$ 1:3-Diphenyl-5-isopropyl-2-thiobarbituric acid (WHITELEY and MOUNTAIN), P., 121.

C₂₀ Group.

- $C_{20}H_{12}N_2$ α -N-6
|
 β -CH-5
-Naphthaquinacridine, and its aurichloride (SENIER and COMPTON), T., 1631; P., 220.

- $C_{20}H_{12}N_2$ β -N-6
|
-Naphthaquinacridine, and its salicylate (SENIER and
a-CH-5
COMPTON), T., 1632 ; P., 220.
- $C_{20}H_{16}O_7$ Tetramethoxy- α -brazanquinone (PERKIN and ROBINSON), T., 399.
- $C_{20}H_{19}N_5$ Benzeneazobenzeneazodimethylaniline, and its hydrochloride
(HEWITT and THOLE), T., 1395 ; P., 208.
- $C_{20}H_{20}O_2$ 4-Ethoxy-3:4-diphenyl-2-methyl- Δ^2 -cyclopentenone (GRAY), T.,
2134.
- 2-Methoxy-3:4-diphenyl-5:5-dimethyl- Δ^2 -cyclopentenone (GRAY), T.,
2147.
- $C_{20}H_{22}O_3$ Ethyl α -benzoyl- β -phenyl- α -ethylpropionate (HOPE and PER-
KIN), T., 2050.
- $C_{20}H_{26}O_5$ Eugenyl hydrogen camphorate, rotatory power of (HILDITCH),
T., 336.
- iso*Eugenyl hydrogen camphorate, and its rotatory power (HILDITCH),
T., 337.
- $C_{20}H_{28}O_4$ *l*-Menthyl *d*-, *l*-, and *dl*-acetylmandelate (MCKENZIE and HUM-
PHRIES), T., 1109, 1111.
- $C_{20}H_{28}O_6$ Cynotoxin (FINNEMORE), P., 77.

20 III

- $C_{20}H_{14}O_4N_2$ $\alpha\delta$ -Dicyano- $\beta\gamma$ -diphenyl- $\Delta\beta$ -butene- $\alpha\delta$ -dicarboxylic acid, and
its potassium and sodium salts (HAWORTH), T., 486.
- $C_{20}H_{16}ON_2$ 3-Keto-2:5-distyryl-3:4-dihydro-1:4-diazine, and its hydrochloride
(McCOMBIE and PARRY), T., 589 ; P., 95.
- $C_{20}H_{16}O_2N_2$ Disalicylidene-*p*-phenylenediamine (SENIER and SHEPHEARD),
T., 1950.
- $C_{20}H_{16}O_2N_4$ Benzeneazobenzeneazophenyl acetate (HEWITT and THOLE),
T., 1397 ; P., 208.
- $C_{20}H_{17}O_1N$ Nitro- α -anhydrotrimethylbrazilone methyl ether (PERKIN
and ROBINSON), T., 394.
- $C_{20}H_{19}O_4P$ Phenyl di-*p*-tolyl phosphate (LUFF and KIPPING), T., 2002.
- $C_{20}H_{23}O_4N$ 1:2-Dihydropapaverine, (and +3H₂O) and its hydrochloride
(PYMAN), T., 1620 ; P., 217.
- $C_{20}H_{25}O_4N$ Tetrahydropapaverine, and its salts (PYMAN), T., 1614 ; P., 217.
- $C_{20}H_{26}O_5S$ Eugenyl camphor- β -sulphonate, and its rotatory power (HIL-
DITCH), T., 338.
- iso*Eugenyl camphor- β -sulphonate, and rotatory power of (HILDITCH),
T., 338.
- $C_{20}H_{27}O_4N$ Dihydroxydi-*o*-tolyl oxydipropylamine (BOYD and KNOWL-
TON), T., 1805 ; P., 235.
- $C_{20}H_{27}O_{11}N$ Amygdalin, hydrolysis of (AULD), T., 927 ; P., 62 ; (WALKER and
KRIEBLE), T., 1369 ; P., 203.
- iso*Amygdalin, experiments on (TUTIN), T., 663 ; P., 118.
- $C_{20}H_{29}O_3Hg_3$ Substance, from action of potassium hydroxide on $C_{30}H_{42}O_3I_2Hg_4$
(MARSH and STRUTHERS), T., 1787.
- $C_{20}H_{30}O_3Hg_2$ Mercuricamphor oxide (MARSH and STRUTHERS), T., 1785.
- $C_{20}H_{30}O_4N_2$ Fumaroyltropeine, and its hydrochloride and hydriodide (JOWETT
and PYMAN), T., 1026.
- $C_{20}H_{31}O_4P$ Dicapthorylphosphinic acid (MORGAN and MOORE), P., 310.
- $C_{20}H_{32}O_6N_2$ Tartryltropeine, and its salts (JOWETT and PYMAN), T., 1026.
- $C_{20}H_{33}O_2N$ *l*-Menthylamine α - β -phenyl- α -methylpropionate (PICKARD
and YATES), T., 1019 ; P., 152.

20 IV

- $C_{20}H_{14}O_2N_2Br_2$ 5:5'-Dibromodisalicicylidene-*p*-phenylenediamine (SENIER and SHEPHEARD), T., 1953.
 $C_{20}H_{16}ON_2Br_4$ 3-Keto-2:5-distyryl-3:4-dihydro-1:4-diazine tetrabromide (McCOMBIE and PARRY), T., 590.

C₂₁ Group.

- $C_{21}H_{16}O_8$ Diacetylrhein ethyl ester (ROBINSON and SIMONSEN), T., 1092; P., 76.
 $C_{21}H_{20}O_3$ 4-Acetoxy-3:4-diphenyl-5:5-dimethyl- Δ^2 -cyclopentenone (GRAY), T., 2137.
 $C_{21}H_{20}O_{12}$ Quercimeritrin, from *Gossypium herbaceum*, and its potassium salt (PERKIN), T., 2185; P., 291.
*iso*Quercitrin, from *Gossypium herbaceum* (PERKIN), T., 2190; P., 292.
 $C_{21}H_{20}O_{13}$ Gossypitrin, from *Gossypium herbaceum* (PERKIN), T., 2189; P., 292.
 $C_{21}H_{24}N_8$ Bistolnenezotolylenediamine (*Vesuvine*), rate of formation of (VELEY), T., 1197; P., 175.

21 III

- $C_{21}H_{13}O_4N$ 3:4-Dibenzoyloxybenzoxynitrile (EWINS), T., 1488.
 $C_{21}H_{17}O_3N$ Carbanilido-*l*-benzoin (WREN), T., 1586.
 $C_{21}H_{17}O_8N$ Nitroacetyl- α -anhydrotrimethylbrazilone (PERKIN and ROBINSON), T., 393.
 Nitroacetyl- β -anhydrotrimethylbrazilone (PERKIN and ROBINSON), T., 397.
 $C_{21}H_{19}O_3N$ Ethyl α -cyano- β -benzoyl- α -styrylpropionate (HAWORTH), T., 484.
 $C_{21}H_{20}O_4N_2$ Benzoyl derivative of ethyl 2:6-dicyano-1:1:5-trimethyl- Δ^2 -*cyclohexadien-3-ol-6-carboxylate* (+H₂O) (GARDNER and HAWORTH), T., 1959.
 $C_{21}H_{21}O_3N$ Oxime of 4-acetoxy-3:4-diphenyl-5:5-dimethyl- Δ^2 -cyclopentenone (GRAY), T., 2147.
 $C_{21}H_{21}O_3Sb$ *o*-, *m*-, and *p*-Tolyl antimonite (MACKEY), T., 608; P., 98.
 $C_{21}H_{23}ON$ β -Naphthylamino-*d*-methylenecamphor, rotatory power of (POPE and READ), T., 178; P., 19.
 $C_{21}H_{27}ON$ *ac*-Tetrahydro- β -naphthylamino-*d*-methylenecamphor (POPE and READ), T., 180.
 $C_{21}H_{27}O_3N$ Laudanosine, oxidation of (PYMAN), T., 1266; P., 190; hydriodide of (PYMAN), T., 1616.
 $C_{21}H_{31}O_2N$ *l*-Menthylamine *d*- Δ^3 -dihydro-2-naphthoate (PICKARD and YATES), T., 1014; P., 152.
 $C_{21}H_{33}O_2N$ *l*-Menthylamine *d*-phenylallylacetate (PICKARD and YATES), T., 1016; P., 152.
 $C_{21}H_{34}O_2N_2$ 5-Imino-2-cyano-1:3-dimethyl-6-amyl-3-hexyl- Δ^6 -cyclohexene-2-carboxylic acid (GARDNER and HAWORTH), T., 1964.
 $C_{21}H_{35}O_2N$ *l*-Menthylamine *d*- β -phenyl- α -ethylpropionate (PICKARD and YATES), T., 1018; P., 152.
l-Menthylamine α -phenylvalerate (PICKARD and YATES), T., 1017; P., 152.

21 IV

- $C_{21}H_{16}O_2N_2S$ Ethyl 3-cyano-4-keto-2-phenylimino-5-benzylidenetetrahydrothiophen-3-carboxylate (RUHEMANN), T., 121.

- $C_{21}H_{16}O_3N_4S$ Pyridine β -1:3-diphenyl-2-thioviolurate (WHITELEY and MOUNTAIN), P., 122.
- $C_{21}H_{16}O_4N_4S$ Ethyl 3-cyano-4-keto-2-phenylimino-5-salicylidene-tetrahydrothiophen-3-carboxylate (RUHEMANN), T., 121.
- $C_{21}H_{20}O_3N_4S$ Piperidine β -1:3-diphenyl-2-thioviolurate (WHITELEY and MOUNTAIN), P., 122.

C_{22} Group.

- $C_{22}H_{16}O_2$ *cis*- $\alpha\beta$ -Dibenzoylstyrene, refraction of, and action of isoamylamine on (SMEDLEY), T., 219; P., 17.
- $C_{22}H_{18}O_2$ Dibenzylphthalide, formation from magnesium benzyl chloride and diethyl phthalate (SHIBATA), T., 1454.
- $C_{22}H_{18}O_9$ Triacetylchrysoeriol (TUTIN and CLEWER), T., 85; P., 12.
- $C_{22}H_{23}N_5$ *o*-Tolueneazo-*o*-tolueneazodimethylaniline, and its hydrochloride (HEWITT and THOLE), T., 1396; P., 208.
- $C_{22}H_{24}O_4$ Menthyl piperate, and its rotatory power (HILDITCH), T., 1572; P., 214.
- $C_{22}H_{30}O_4$ Menthyl $\alpha\beta$ - and $\beta\gamma$ -hydropiperate, and their rotatory powers (HILDITCH), T., 1572; P., 214.
- $C_{22}H_{32}O_4$ Menthyl piperonylbutyrate, and its rotatory power (HILDITCH), T., 1573; P., 214.
- $C_{22}H_{38}O_4$ Dimenthyl oxalate, and its rotatory power (HILDITCH), T., 1579; P., 214.

22 III

- $C_{22}H_{12}O_6Cl_2$ 7:10-Dichloro-1:6-diacetoxynaphthacenequinone (HARROP, NORRIS, and WEIZMANN), T., 284.
- $C_{22}H_{17}ON_3$ Phenylhydrazone of diketodiphenylpyrroline (RUHEMANN), T., 989.
- $C_{22}H_{17}O_4N$ ω -Benzoylamino-*p*-benzoyloxyacetophenone (TUTIN, CATON, and HANN), T., 2120.
- $C_{22}H_{19}O_3N$ α -*p*-Benzoyloxy-*N*-benzoylphenylethylamine (TUTIN, CATON, and HANN), T., 2123.
- $C_{22}H_{19}O_4N$ Dibenzoyl derivative of β -*p*-dihydroxy- β -phenylethylamine (TUTIN, CATON, and HANN), T., 2121.
- $C_{22}H_{19}O_9N$ Nitroacetyl- α -anhydrotetramethylhaematoxylone (PERKIN and ROBINSON), T., 398.
- $C_{22}H_{20}O_2N_2$ 2:2'-Dimethoxydibenzylidene-*p*-phenylenediamine, and its hydrochloride (SENIER and SHEPHEARD), T., 1951.
- 2:2'-Dihydroxy-5:5'-dimethyldibenzylidene-*p*-phenylenediamine (SENIER and SHEPHEARD), T., 1953.
- $C_{22}H_{21}ON_3$ ω -Phenylacetylaminooacetophenonephenylhydrazone (ROBINSON), T., 2170; P., 295.
- $C_{22}H_{23}O_2N_2$ Diacetyl-6-*o*-tolyl-1-methyl-5:7-naphthylenediamine (BEST and THORPE), T., 267.
- Diacetyl-6-*m*-tolyl-2-methyl-5:7-naphthylenediamine (BEST and THORPE), T., 269.
- Diacetyl-7-*p*-tolyl-2-methyl-6:8-naphthylenediamine (BEST and THORPE), T., 272.
- $C_{22}H_{22}O_2N_6$ Azoantipyrene (FORSTER and MÜLLER), T., 2076.
- $C_{22}H_{23}O_7N$ Chloroxylonine, from *Chloroxylon swietenia*, and its salts (AULD), T., 966; P., 148.
- $C_{22}H_{25}O_{10}N$ Tetra-acetyl-*l*-mandelonitrile glucoside (POWER and MOORE), T., 259; P., 27.

- $C_{22}H_{39}O_4N$ *N*-Ethyltetrahydropapaverine, and its picrate (PYMAN), T., 1744.
 $C_{22}H_3O_3Si_2$ Benzyl-diethoxysilicyl oxide (MARTIN and KIPPING), T., 310.

22 IV

- $C_{22}H_{10}ON_4Br_6$ Bis-2':4':6'-tribromobenzeneazo- α -naphthol (MITCHELL and SMITH), T., 1437; P., 210.
 $C_{22}H_{15}O_4N_5S$ 1:3-Diphenyl-2-thioalloxan-*p*-nitrophenylhydrazone (WHITELEY and MOUNTAIN), P., 122.
 $C_{22}H_{15}O_3N_4S$ 1:3-Diphenyl-2-thioalloxanphenylhydrazone (WHITELEY and MOUNTAIN), P., 122.
 $C_{22}H_{22}O_3NP$ α - and β -*dl*- and α - and β -*d*-Hydriindamide of phenyl-*p*-tolyl-phosphoric acid (LUFF and KIPPING), T., 2006.

 C_{23} Group.

- $C_{23}O_{20}O_8$ Diacetoxytrimethoxy- α -brazan (PERKIN and ROBINSON), T., 396.
 $C_{23}H_{32}O_3$ Glycerol dithymyl ether (BOYD and MARLE), T., 1808; P., 235.
 $C_{23}H_{40}O_4$ Dimethyl malonate, and its rotatory power (HILDITCH), T., 1579; P., 214.
 Ipuranol, isolation of, from *Apocynum androsaemifolium* (MOORE), T., 737; P., 85.

23 III

- $C_{23}H_{17}O_3N_3$ Phenylhydrazone of 2:3-diketo-4-phenyl-5-piperonylpyrrolidine (RUHEMANN), T., 1609.
 $C_{23}H_{15}O_3N_2$ Benzamide of β -benzoylaminoacetic acid (RUHEMANN), T., 988.
 $C_{23}H_{15}ON_3$ Phenylhydrazone of 2:3-diketo-4-phenyl-5-*o*-tolylpyrroline (RUHEMANN), T., 991.
 Phenylhydrazone of 2:3-diketo-4-phenyl-5-*m*-tolylpyrroline (RUHEMANN), T., 1606.
 Phenylhydrazone of 2:3-diketo-4-phenyl-5-*p*-tolylpyrroline (RUHEMANN), T., 1607.
 $C_{23}H_{26}ON_2$ Malachite-green (carbinol-form), rate of reaction of, with acid and alkali (SIDGWICK and MOORE), T., 889; P., 123.
 $C_{23}H_{26}O_2N_4$ Camphordiazodiphenylcarbamide, and its isomeride (FORSTER and GARLAND), T., 2059.
 $C_{23}H_{28}ON_2$ Bis(2- β -methylaminoethylbenzylidene)acetone, and its dihydride (PYMAN), T., 1750.
 $C_{23}H_{31}O_4N$ *N*-Propyltetrahydropapaverine, and its picrate (PYMAN), T., 1747.

23 IV

- $C_{23}H_{14}O_3NCl$ 7(10)-Chloro-10(7)-anilino-1-hydroxynaphthacenequinone (HARROP, NORRIS, and WEIZMANN), T., 285.
 $C_{23}H_{15}O_4N_3S$ 1:3-Diphenyl-5-*o*-nitrobenzylidene-2-thiobarbituric acid (WHITELEY and MOUNTAIN), P., 122.
 $C_{23}H_{16}O_2N_2S$ 1:3-Diphenyl-5-benzylidene-2-thiobarbituric acid (WHITELEY and MOUNTAIN), P., 121.
 $C_{23}H_{16}O_2N_2S$ 1:3-Diphenyl-5-benzyl-2-thiobarbituric acid (WHITELEY and MOUNTAIN), P., 122.
 $C_{23}H_{21}O_2NS$ Diethyl 4-keto-2-phenylimino-5-benzylidenetetrahydrothiophen-3-dicarboxylate (RUHEMANN), T., 122.
 $C_{23}H_{21}O_2NS$ Diethyl 4-keto-2-phenylimino-5-salicylidenetetrahydrothiophen-3-dicarboxylate (RUHEMANN), T., 122.

- $C_{23}H_{26}O_4NS$ Camphor- β -sulphonyl-*p*-benzoylanilide, and rotatory power of (HILDITCH), T., 339.
 $C_{23}H_{32}O_3NP$ α - and β -*l*-Menthylamide of phenyl-*p*-tolylphosphoric acid (LUFF and KIPPING), T., 2008.

C₂₄ Group.

- $C_{24}H_{18}O_2$ Benzylideneanhydroacetonebenzil, isomeride of (GRAY), T., 2143.
 3:4-Diphenyl-5-benzylidene- Δ^2 -cyclopenten-1-one-2-ol, isomeric forms of (GRAY), T., 2144.
 $C_{24}H_{20}O_{10}$ Triacetyl-xanthoeridol (TUTIN and CLEWER), T., 85; P., 12.
 $C_{24}H_{24}O_4$ 2:6:6-Triacetyl-1:5-diphenylcyclohexan-3-one (RUHEMANN), T., 114.
 $C_{24}H_{26}O_8$ Tetra-acetyl derivative of pinacone, from *p*-hydroxyacetophenone (TUTIN, CATON, and HANN), T., 2122.
 $C_{24}H_{22}O_4$ Dimenthyl succinate, and its rotatory power (HILDITCH), T., 1579; P., 214.

24 III

- $C_{24}H_{16}O_4N_2$ Phthalylmandelonitrile (FRANCIS and DAVIS), T., 1407.
 $C_{24}H_{16}O_2N_3$ Benzoylmethyl-*p*-aminobenzeneazo- β -naphthol (MORGAN and ALCOCK), T., 1325.
 $C_{24}H_{20}N_3As$ Base, from arsenious chloride and aniline (MORGAN and MICKLETHWAIT), T., 1474.
 $C_{24}H_{25}O_{10}N$ Ethyl nitrodiphenyltetracarboxylate (CROSSLEY and HAMP-SHIRE), P., 163.
 $C_{24}H_{32}O_4N_2$ Di-*p*-toluidine camphorate, and its rotatory power (HILDITCH), T., 337.
 Plthaloyltropeine, and its salts (JOWETT and PYMAN), T., 1030.

24 IV

- $C_{24}H_{15}O_6N_9S_3$ Benzene-1:3:5-trisulphonyltri-*p*-phenylenediazoimide (MORGAN and PICKARD), P., 300.
 $C_{24}H_{18}O_3N_4Hg$ Bisbenzeneazo- α -naphthol mercuriacetate (MITCHELL and SMITH), T., 1435; P., 209.
 $C_{24}H_{24}O_4N_3As$ Triacetylaminotriphenylarsine oxide (MORGAN and MICKLETHWAIT), T., 1475.
 $C_{24}H_{24}O_6N_6S_3$ Benzene-1:3:5-trisulphonyltri-*p*-phenylenediamine (MORGAN and PICKARD), P., 300.

C₂₅ Group.

- $C_{25}H_{18}O$ 3:4-Diphenyl-5-benzylidene-2-methylene- Δ^3 -cyclopentenone (GRAY), T., 2136.
 $C_{25}H_{30}O_4$ *l*-Menthyl *dl*-benzoylmandelate (MCKENZIE and HUMPHRIES), T., 1112.
 $C_{25}H_{44}O_4$ Dimenthyl glutarate, and its rotatory power (HILDITCH), T., 1579; P., 214.

25 III

- $C_{25}H_{15}O_3N$ Diphenylpropiolylbenzamide (RUHEMANN), T., 987.
 $C_{25}H_{21}O_2N_3$ Benzoylethyl-*p*-aminobenzeneazo- β -naphthol (MORGAN and ALCOCK), T., 1325.
 $C_{25}H_{22}ON_2$ Phenylbenzylhydrazide of benzylfurfuraldehyde (FENTON and ROBINSON), T., 1336; P., 193.

- $C_{25}H_{23}ON_3$ Phenylhydrazone of 2:3-diketo-4-phenyl-5-cumylpyrroline (RUEHMANN), T., 1607.
- $C_{25}H_{24}ON_2$ Phenylhydrazone of 3:4-diphenyl-5:5-dimethyl- Δ^2 -cyclopenten-1-one-2-ol (GRAY), T., 2147.
- $C_{25}H_{32}O_3N_2$ Carbonate of 3-cyano-1:2:4-trimethyl-4-ethyl- $\Delta^{1,5}$ -cyclohexadien-6-ol (GARDNER and HAWORTH), T., 1960.

25 IV

- $C_{25}H_{16}O_3NCl$ 7(10)-Chloro-10(7)-*p*-toluidino-1-hydroxynaphthacenequinone (HARROP, NORRIS, and WEIZMANN), T., 285.
- $C_{25}H_{18}O_2N_2S$ 1:3-Diphenyl-5-cinnamylidene-2-thiobarbituric acid (WHITELEY and MOUNTAIN), P., 122.
- $C_{25}H_{35}O_6NS$ Benzoyltropeine *d*-camphorsulphonate (BARROWCLIFF and TUTIN), T., 1972; P., 257.
- Benzoyl- ψ -tropeine *d*-camphorsulphonate (BARROWCLIFF and TUTIN), T., 1972; P., 257.

25 V

- $C_{25}H_{34}O_6NBrS$ Benzoyl- ψ -tropeine *d*-bromocamphorsulphonate (+3H₂O) (BARROWCLIFF and TUTIN), T., 1972; P., 257.

 C_{26} Group.

- $C_{26}H_{18}O$ 1:1-Diphenyl-3-phenylenephthalan (SHIBATA), T., 1454; P., 209.
- $C_{26}H_{18}O_2$ $\alpha\gamma$ -Diphenyl- γ -1-naphthylallene- α -carboxylic acid (LAPWORTH and WECHSLER), P., 307.
- $C_{26}H_{20}O_3$ 2-Acetoxy-3:4-diphenyl-5-benzylidene- Δ^2 -cyclopentenone, isomeric forms of (GRAY), T., 2145.
- 4-Acetoxy-3:4-diphenyl-5-benzylidene- Δ^2 -cyclopentenone (GRAY), T., 2137.
- $C_{26}H_{28}O_6$ Diethyl 6-acetyl-1:5-diphenylcyclohexan-3-one-2:6-dicarboxylate, and its sodium derivative (RUEHMANN), T., 112.
- $C_{26}H_{42}O_4$ Dimethyl muconate, and its rotatory power (HILDITCH), T., 1571; P., 214.
- $C_{26}H_{44}O_4$ Dimethyl $\alpha\beta$ - and $\beta\gamma$ -hydromuconate, and their rotatory powers (HILDITCH), T., 1572; P., 214.
- $C_{26}H_{46}O_4$ Dimethyl adipate, and its rotatory power (HILDITCH), T., 1572; P., 214.

26 III

- $C_{26}H_{20}O_3N_4$ Benzoyl-*p*-aminobenzene diazo-oxide (MORGAN and ALCOCK), T., 1327.
- $C_{26}H_{26}O_4N_2$ Trimethoxy- α -brazotoluquinioxaline (PERKIN and ROBINSON), T., 395.
- $C_{26}H_{21}O_2N_5$ Dibenzoyl-4:4'-diaminodiazaminobenzene (MORGAN and ALCOCK), T., 1326.
- $C_{26}H_{28}O_6Br_2$ Dibromo-derivative of diethyl 6-acetyl-1:5-diphenylcyclohexan-3-one-2:6-dicarboxylate (RUEHMANN), T., 113.
- $C_{26}H_{31}O_7N$ Indican (THOMAS, BLOXAM, and PERKIN), T., 824; P., 126.
- $C_{26}H_{32}O_2N_2$ *p*-Phenylenebisiminocamphor (FORSTER and THORNLEY), T., 955.
- $C_{26}H_{32}O_6N_2$ Di-*p*-aminoacetophenone camphorate (+1½H₂O), and its rotatory power (HILDITCH), T., 337.
- $C_{26}H_{36}O_4N_2$ Ethyl $\alpha\delta$ -diethylanilinoadipate (LE SUEUR), T., 278.

26 IV

$C_{26}H_{48}O_6N_2S_2$ *l*-Menthylamine benzenedisulphonate (KIPPING and MARTIN), T., 492; P., 67.

26 V

$C_{26}H_{48}O_3N_3Si$ *l*-Menthylamine *dl*-benzylethylpropylisobutylsilicane-sulphonate, (and +2H₂O) (KIPPING and DAVIS), T., 74; P., 9.

C₂₇ Group.

- $C_{27}H_{44}O_2$ 4-Ethoxy-3:4-diphenyl-5-benzylidene-2-methyl- Δ^2 -cyclopentenone (GRAY), T., 2135.
- $C_{27}H_{26}O_{11}$ Tetra-acetyleriodonol (TUTIN and CLEWER), T., 86; P., 12.
- $C_{27}H_{27}N_3$ 6-Amino-5-*o*-tolyl-2:4-di-*o*-methylbenzylpyrimidine (BEST and THORPE), T., 266.
- 6-Amino-5-*m*-tolyl-2:4-di-*m*-methylbenzylpyrimidine, and its hydrochloride (BEST and THORPE), T., 268.
- 6-Amino-5-*p*-tolyl-2:4-di-*p*-methylbenzyl-pyrimidine, and its hydrochloride (BEST and THORPE), T., 271.
- $C_{27}H_{44}O$ Homoandrosterol (MOORE), T., 740; P., 85.
- $C_{27}H_{44}O_4$ Acid, from oxidation of cholesterol, (DORÉE), T., 640; P., 88.
- $C_{27}H_{44}O_5$ Cholestenone ozonide (DORÉE), T., 643; P., 88.
- $C_{27}H_{44}O_7$ Ozonide of acid $C_{27}H_{44}O_4$, from cholesterol (DORÉE), T., 641; P., 88.
- $C_{27}H_{44}O_{11}$ Ozonide of acid $C_{27}H_{44}O_4$, from cholesterol (DORÉE), T., 642; P., 88.
- $C_{27}H_{46}O$ α -Cholestanol, action of ozone on (DORÉE), T., 647; P., 88.
- β -Cholestanone, action of bromine on (DORÉE), T., 648.
- Cholesterol, chemistry of (DORÉE), T., 633; P., 88.
- Coprostanone, action of bromine on, and reaction of, with phenylhydrazine (DORÉE), T., 648.
- Phytosterol, from *Eballium elaterium* (POWER and MOORE), T., 1987; P., 260.
- Phytosterol, from bark of *Prunus serotina* (POWER and MOORE), T., 246; P., 27.
- Phytosterol, from wheat germ, action of ozone on (DORÉE), T., 649.
- $C_{27}H_{46}O_7$ β -Cholestanone ozonide (DORÉE), T., 645; P., 88.
- $C_{27}H_{46}O_8$ Coprostanone ozonide (DORÉE), T., 647; P., 88.
- $C_{27}H_{48}O$ Coprosterol, chemistry of (DORÉE), T., 638; P., 88.
- $C_{27}H_{48}O_4$ Dimethyl pimelate, and its rotatory power (HILDITCH), T., 1579; P., 214.
- β -Cholestanol ozonide (DORÉE), T., 644; P., 88.
- Coprosterol ozonide (DORÉE), T., 645; P., 88.
- $C_{27}H_{48}O_7$ ψ -Coprosterol ozonide (DORÉE), T., 646; P., 88.

27 III

- $C_{27}H_{20}O_5N_2$ Tetramethoxy- α -brazotolquinoxaline (PERKIN and ROBINSON), T., 399.
- $C_{27}H_{24}O_2N_4$ Dicarbanilindiphenylmethylenediamine (SENIER and SHEPHEARD), T., 496.
- $C_{27}H_{24}N_4S_2$ Dithiocarbanilindiphenylmethylenediamine (SENIER and SHEPHEARD), T., 498.
- $C_{27}H_{27}O_5N$ *N*-Benzoyl-1:2-dihydropapaverine (PYMAN), T., 1621.
- $C_{27}H_{28}O_5N$ *N*-Benzoyltetrahydropapaverine (PYMAN), T., 1617; P., 217.
- $C_{27}H_{33}O_6N_5$ Brucine α - and *l*- α -triazobutyrate (FORSTER and MÜLLER), T., 195.

- $C_{27}H_{34}ON_2$ Brilliant-green (carbinol-form), rate of reaction of, with acid and alkali (SIDGWICK and MOORE), T., 889; P., 123.
 $C_{27}H_{36}O_2N_2$ Bis(4:5-dimethoxy-2- β -methylaminoethylbenzylidene)acetone (+4H₂O), and its dihydrochloride (PYMAN), T., 1274; P., 190.
 $C_{27}H_{44}OBr_2$ Dibromocoprostanone (DORÉE), T., 649.

27 IV

- $C_{27}H_{38}O_3NBr$ Bromo-*N*-benzoyltetrahydropapaverine (PYMAN), T., 1617.
 $C_{27}H_{39}O_2NS$ *d*- and *l*-Hyoscyamine *d*-camphorsulphonate (BARROWCLIFF and TUTIN), T., 1974; P., 257.

C₂₈ Group.

- $C_{28}H_{30}O_2$ *cis*- and *trans*-*s*-Dibenzoylstilbene, refraction of (SMEDLEY), T., 220; P., 17.
 $C_{28}H_{20}O_4$ 5:8-Diphenoxy-1:2-, -1:3-, and -1:4-dimethylantraquinone (HARROP, NORRIS, and WEIZMANN), T., 1315, 1317, 1319.
 $C_{28}H_{36}O_6$ Apocynamarin (+2H₂O) (MOORE), P., 750; P., 85.
 $C_{28}H_{50}O_4$ Dimethyl suberate, and its rotatory power (HILDITCH), T., 1579; P., 214.

28 III

- $C_{28}H_{12}O_3Cl_4$ Tetrachloro- α -naphthafluoran (HARROP, NORRIS, and WEIZMANN), T., 286.
 $C_{28}H_{20}O_2N_2$ 2:2'-Dihydroxydi- α -naphthylidene-*p*-phenylenediamine (SENIER and SHEPHEARD), T., 1955.
 $C_{28}H_{20}O_2S_2$ 5:8-Diphenylthiol-1:2-, -1:3-, and -1:4-dimethylantraquinone (HARROP, NORRIS, and WEIZMANN), T., 1316, 1318, 1319.
 $C_{28}H_{22}O_2N_2$ 5:8-Dianilino-1:2-, -1:3-, and -1:4-dimethylantraquinone (HARROP, NORRIS, and WEIZMANN), T., 1315, 1317, 1319.
 $C_{28}H_{24}O_3N_4$ Benzoylmethyl-*p*-aminobenzene diazo-oxide (MORGAN and ALCOCK), T., 1327.
 $C_{28}H_{25}O_2N_5$ Dibenzoyldimethyl-4:4'-diaminodiazaminobenzene (MORGAN and ALCOCK), T., 1326.

C₂₉ Group.

- $C_{29}H_{24}O$ 1:1-Dibenzyl-3-benzylidenephthalan (SHIBATA), T., 1455; P., 209.
 $C_{29}H_{46}O_2$ Acetylhomandrosterol (MOORE), T., 740; P., 85.
 $C_{29}H_{52}O_4$ Dimethyl azelate, and its rotatory power (HILDITCH), T., 1579; P., 214.

29 III

- $C_{29}H_{23}O_5N$ β -*p*-Dibenzoyloxy-*N*-benzoyl- β -phenylethylamine (TUTIN, CATON, and HANN), T., 2121.
 $C_{29}H_{25}O_2N_4$ Dicarbanilinodi-*p*-tolylmethylenediamine (SENIER and SHEPHEARD), T., 500.
 $C_{29}H_{25}N_4S_2$ Dithiocarbo-*o*- and -*p*-toluidinodiphenylmethylenediamine (SENIER and SHEPHEARD), T., 499, 500.
 Dithiocarbanilinodi-*p*-tolylmethylenediamine (SENIER and SHEPHEARD), T., 502.
 $C_{29}H_{34}O_6N_2$ Brucine sorbate (+1½H₂O), and its rotatory power (HILDITCH), T., 1574; P., 214.
 $C_{29}H_{36}O_6N_2$ Brucine $\beta\gamma$ -hexenoate, and its rotatory power (HILDITCH), T., 1574; P., 214.

$C_{29}H_{38}O_6N_2$ Brucine *n*-hexoate (+3H₂O), and its rotatory power (HILDITCH), T., 1574; P., 214.

$C_{21}H_{40}O_5N_2$ Bis(4:5-dimethoxy-2- β -ethylaminoethylbenzylidene)acetone, and its hydrochloride (PYMAN), T., 1747.

29 IV

$C_{29}H_{29}O_4N_4S$ 5-Benzeneazo-1:3-diphenyl-5-benzyl-2-thiobarbituric acid (WHITELEY and MOUNTAIN), P., 122.

C₃₀ Group.

$C_{30}H_{50}O$ Androsterol (+H₂O) (MOORE), T., 739; P., 85.

$C_{30}H_{54}O_4$ Dimethyl sebacate, and its rotatory power (HILDITCH), T., 1580; P., 214.

30 III

$C_{30}H_{28}O_3N_4$ Benzoylethyl-*p*-aminobenzene diazo-oxide (MORGAN and ALCOCK), T., 1328.

$C_{30}H_{29}O_2N_5$ Dibenzoyldiethyl-4:4'-diaminodiazaminobenzene (MORGAN and ALCOCK), T., 1326.

$C_{30}H_{39}O_6N$ Trihydroxytri-*o*-tolylxytripropylamine, and its salts (BOYD and KNOWLTON), T., 1806; P., 235.

$C_{30}H_{39}O_7N$ Trihydroxytri-*o*-tolylxytripropylamine oxide (BOYD and KNOWLTON), T., 1806.

$C_{30}H_{44}O_{10}N_2$ Substance, from reduction of myristicynlideneaminoacetal (SALWAY), T., 1212.

$C_{30}H_{47}O_5As$ Tricamphorylarsinic acid, and its silver salt (MORGAN and MICKLETHWAIT), T., 1476; P., 212.

$C_{30}H_{50}O_{19}N_4$ Chitin, ($C_{30}H_{50}O_{19}N_4$)_n, polarimetric method of identifying, and constitution of (IRVINE), T., 564; P., 89.

30 IV

$C_{30}H_{18}O_3N_2Cl_2$ 8:9-Dichloro-7:10-dianilino-1-hydroxynaphthacenequinone (HARROP, NORRIS, and WEIZMANN), T., 288.

$C_{30}H_{29}O_4N_2Br$ Strychnine α -bromocinnamate, (and +H₂O) (JAMES and SUBBOROUGH), T., 1539.

Strychnine α -bromo*allo*cinnamate, (and +H₂O) (JAMES and SUBBOROUGH), T., 1538.

$C_{30}H_{42}O_3I_2Hg_4$ Substance, from camphor and K₂HgI₄ (MARSH and STRUTHERS), T., 1781.

$C_{30}H_{45}O_3Cl_2Sb$ Tricamphorylstibine chloride (MORGAN, MICKLETHWAIT, and WHITBY), P., 302.

C₃₁ Group.

$C_{31}H_{32}N_4S_2$ Dithiocarbo-*o*- and -*p*-toluidinodi-*p*-tolylmethylenediamine (SENIER and SHEPHEARD), T., 502, 503.

C₃₂ Group.

$C_{32}H_{52}O_2$ Acetylandrosterol (MOORE), T., 739; P., 85.

32 III

$C_{32}H_{40}O_6N_2$ Brucine *d*- and *l*-1-methylcyclohexylidene-4-acetate (PERKIN, POPE, and WALLACH), T., 1795.

- $C_{32}H_{51}O_2Br$ Bromoacetylandrosterol (MOORE), T., 740 ; P., 85.
Substance, from extract of *Apocynum androsacmifolium* and bromine (MOORE), T., 742.

C₂₃ Group.

- $C_{23}H_{49}N$ Coprosterylcarbazole (DORÉE), T., 654 ; P., 88.

33 III

- $C_{23}H_{48}ON_2$ Nitroso-derivative of coprosterylcarbazole (DORÉE), T., 654 ; P., 88.

C₃₄ Group.

- $C_{34}H_{41}O_{18}N$ Hepta-acetylamygdalin, preparation and properties of (TUTIN), T., 665 ; P., 118.

Hepta-acetylneoamygdalin, and resolution and hydrolysis of (TUTIN), T., 666 ; P., 118.

- $C_{34}H_{42}O_6N_2$ Phenylhydrazone of apocynamarin (MOORE), T., 751.

C₃₅ Group.

- $C_{35}H_{28}O_8N_4$ Dicarbonaphthylaminodiphenylmethylenediamine (SENIER and SHEPHEARD), T., 497.

- $C_{35}H_{36}O_8N_2$ Brucine piperate ($+1\frac{1}{2}H_2O$), and its rotatory power (HILDITCH), T., 1574 ; P., 214.

- $C_{35}H_{38}O_8N_2$ Brucine $\alpha\beta$ -hydropiperate ($+4H_2O$), and its rotatory power (HILDITCH), T., 1574 ; P., 214.

Brucine $\beta\gamma$ -hydropiperate ($+3H_2O$), and its rotatory power (HILDITCH), T., 1574 ; P., 214.

- $C_{35}H_{40}O_8N_2$ Brucine piperonylbutyrate ($+4\frac{1}{2}H_2O$), and its rotatory power (HILDITCH), T., 1574 ; P., 214.

C₃₆ Group.

- $C_{36}H_{36}O_6N_2$ Di-*p*-aminobenzophenone camphorate, and its rotatory power (HILDITCH), T., 337.

C₃₇ Group.

- $C_{37}H_{36}O_{18}$ Octa-acetylquercimeritrin (PERKIN), T., 2185 ; P., 291.

37 III

- $C_{37}H_{32}O_2N_4$ Dicarbonaphthylaminodi-*p*-tolylmethylenediamine (SENIER and SHEPHEARD), T., 501.

C₃₈ Group.

- $C_{38}H_{30}O_{10}$ Di- α -anhydrotrimethylbrazilone (PERKIN and ROBINSON), T., 392.

- $C_{38}H_{30}O_{12}$ Trimethoxy- α -brazanquinhydrone (PERKIN and ROBINSON), T., 396.

- $C_{38}H_{32}O_2$ Dehydration product of $\alpha\beta$ -dimethylanhydroacetonebenzil (GRAY), T., 2134.

38 IV

$C_{38}H_{30}O_2N_3As$ Dibenzoyl derivative of base, from arsenious chloride and aniline (MORGAN and MICKLETHWAIT), T., 1475.

$C_{38}H_{32}O_4SSb_2$ Triphenylstibine hydroxysulphate (MORGAN, MICKLETHWAIT, and WHITBY), P., 302.

C₃₉ Group.

$C_{39}H_{30}O_4N_3As$ Tribenzoylamino-triphenylarsine oxide (MORGAN and MICKLETHWAIT), T., 1475.

C₄₂ Group.

$C_{42}H_{34}O_{12}$ Di- α -anhydrotrimethylbrazilone diacetate (PERKIN and ROBINSON), T., 302.

42 III

$C_{42}H_{42}OSi_2$ Tribenzylsilicyl oxide (MARTIN and KIPPING), T., 307; P., 28.

C₄₈ Group.

$C_{48}H_{54}O_{12}N_4$ Dibrucine oxalate (+4½H₂O), and its rotatory power (HILDITCH), T., 1580; P., 214.

C₄₉ Group.

$C_{49}H_{56}O_{12}N_4$ Dibrucine malonate (+3H₂O), and its rotatory power (HILDITCH), T., 1580; P., 214.

C₅₀ Group.

$C_{50}H_{70}O_4I_2Hg_6$ Substance, from interaction of camphor and mercuric and potassium iodides (MARSH and STRUTHERS), T., 1787.

C₅₁ Group.

$C_{51}H_{60}O_{12}N_4$ Dibrucine glutarate (+4H₂O), and its rotatory power (HILDITCH), T., 1580; P., 214.

C₅₂ Group.

$C_{52}H_{58}O_{12}N_4$ Dibrucine muconate (+8H₂O), and its rotatory power (HILDITCH), T., 1573; P., 214.

$C_{52}H_{60}O_{12}N_4$ Dibrucine $\alpha\beta$ -hydromuconate (+5½H₂O), and its rotatory power (HILDITCH), T., 1573; P., 214.

Dibrucine $\beta\gamma$ -hydromuconate (+8H₂O), and its rotatory power (HILDITCH), T., 1573; P., 214.

$C_{52}H_{62}O_{12}N_4$ Dibrucine adipate, and its rotatory power (HILDITCH), T., 1573; P., 214.

C₅₃ Group.

$C_{53}H_{64}O_{12}N_4$ Dibrucine pimelate (+4H₂O), and its rotatory power (HILDITCH), T., 1580; P., 214.

C₅₄ Group.

C₅₄H₆₆O₁₂N₄ Dibrucine suberate (+4½H₂O), and its rotatory power (HILDITCH), T., 1580; P., 214.

C₅₅ Group.

C₅₅H₆₈O₁₂N₄ Dibrucine azelate (+3H₂O), and its rotatory power (HILDITCH), T., 1580; P., 214.

C₅₆ Group.

C₅₆H₇₀O₁₂N₄ Dibrucine sebacate, and its rotatory power (HILDITCH), T., 1580; P., 214.

C₅₈ Group.

C₅₈H₆₂O₁₂N₄ Dibrucine cinnamylidenemalonate (+5H₂O), and its rotatory power (HILDITCH), T., 1574; P., 214.

C₅₈H₆₄O₁₂N₄ Dibrucine phenylpropylidenemalonate (+3H₂O) (HILDITCH), T., 1575; P., 214.

Dibrucine phenylpropenylmalonate (+4H₂O), and its rotatory power (HILDITCH), T., 1574; P., 214.

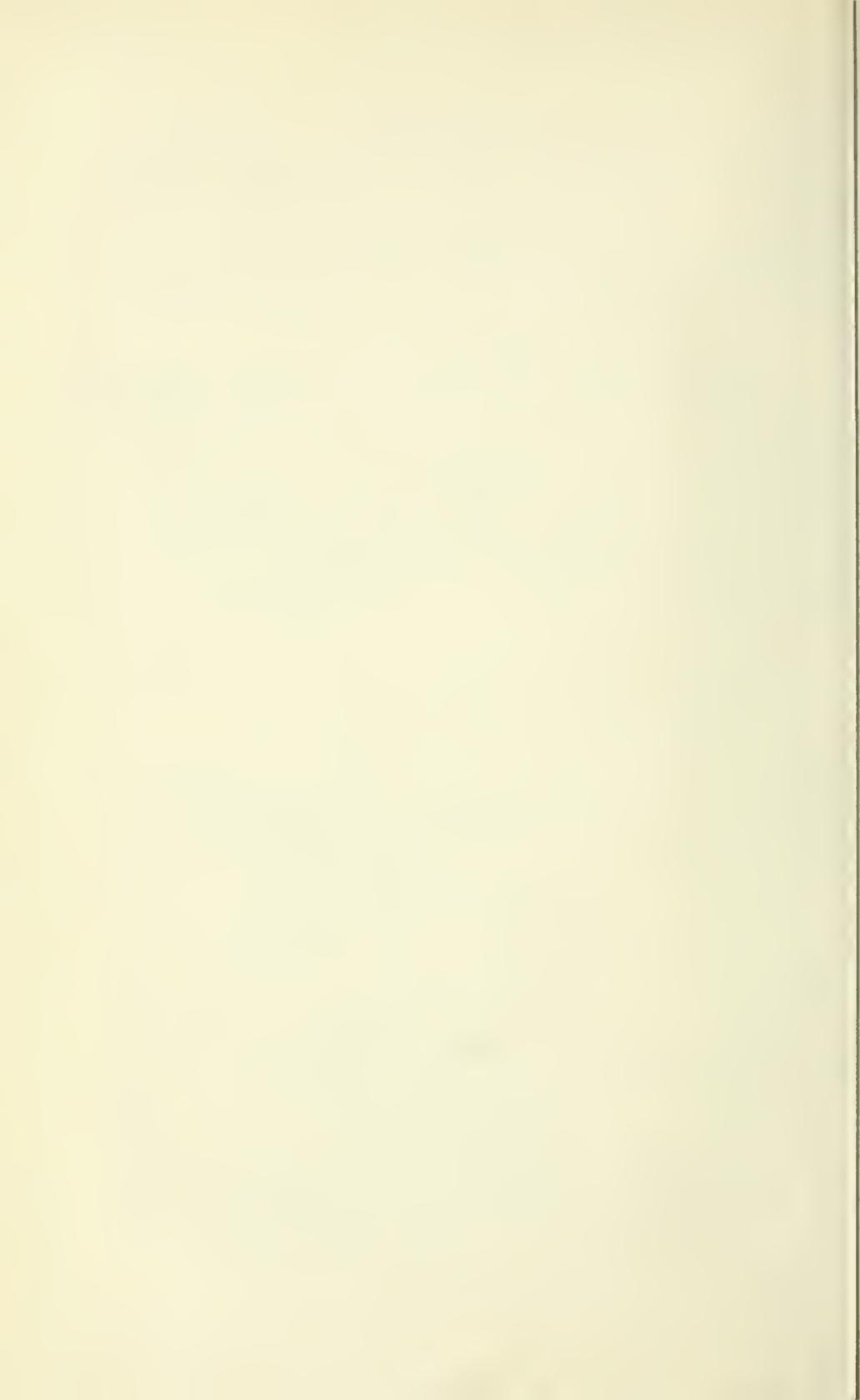
ERRATA.

VOL. XCV (TRANS., 1909).

Page	Line	
116	14	in formula for "CO·C ₆ H ₅ " read "CO·CH ₃ ."
121	15	for "C=65·95" read "C=66·95."
427	7	"Y for H" read "Y for OH."
690	3*	"579" read "594."
711	6	"574" "594."
721	6	"α, β," read "αβ."
722	4*	"OH·Hg·OEt" read "OH·Hg·Et."
723	11	delete "in."
732	1	col. 7 insert "— — —"
732	22	col. 6 for "— —" read "— — —"
864	6*	for "Six grams" read "2·16 grams."
1354	2*	"20" read "40."
1938	12	insert "Density of methyl iodide at $\frac{25^\circ}{25^\circ} = 2\cdot24603$."
1938	20	for "50·8072" read "41·4518."
1951	5	"phototropic" read "thermotropic."
1957	24	omit "-3-carboxylic acid."
1957	25	alter formula to "CMeEt $\left\langle \begin{array}{l} \text{CH(CN)·CME} \\ \text{CH = C(OH)} \end{array} \right\rangle \text{CMe}."$
1958	13	for "acid" read "ester."
1960	7*	"hydroxy-acid" read "dihydrophenol."

* From bottom.







QD
1
C6
v.95
pt.2
cop.3

Chemical Society, London
Journal

1909

Physical &
Applied Sci.
Serials

PLEASE DO NOT REMOVE
CARDS OR SLIPS FROM THIS POCKET

UNIVERSITY OF TORONTO LIBRARY

STORAGE

