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The following are abstracts of papers received during the vacation and published or passed for publication in the *Transactions*.

137. "The action of chromyl chloride on stilbene, styrene, and phenanthrene." By George Gerald Henderson and Thomas Gray.

Each of the hydrocarbons, stilbene, styrene, and phenanthrene, when treated with chromyl chloride in carbon disulphide solution, yields a solid, brown additive compound. These solids are decomposed by water, and oxidation products of the hydrocarbons are liberated. Stilbene is oxidised to benzil, and, with partial decomposition, to benzophenone and benzaldehyde. Styrene yields benzaldehyde as the chief product, together with a trace of phenylacetaldehyde and a small amount of a chlorinated compound. The sole product obtained from phenanthrene was phenanthraquinone.

138. "The stereoisomeric tetramethyl methylglucosides and tetramethyl glucose." By Thomas Purdie and James Colquhoun Irvine.

The pentamethyl glucose (m. p. 42—43°) obtained from tetramethylglucose, either by the silver oxide method of alkylation or by the action of methyl alcohol containing hydrogen chloride (*Trans.*, 1903, 83, 1035), proves to be *tetramethyl-β-methylglucoside*; the stereoisomeric liquid *α-glucoside* is produced simultaneously, but in much

smaller proportion. The β -glucoside is characterised by its lævotatory power, its more rapid hydrolysis by hydrochloric acid, and its susceptibility to the hydrolytic action of emulsin.

In aqueous solution, tetramethyl glucose, like glucose itself, exhibits phenomena of multirotation. The α -form (m. p. 88—89°; $[\alpha]_D^{20} + 100.8^\circ$) is obtained by repeated crystallisation of the crude aldose from petroleum; the β -form (Tanret's γ -form), or at least a mixture containing a large excess of it ($[\alpha]_D^{20} 73.1^\circ$), is produced by heating the α -form above its melting point. The modification, which is stable in solution ($[\alpha]_D^{20} 83.3^\circ$), is apparently a mixture of the two dynamic isomerides. In the solid state, the β -isomeride reverts to the α -form.

Multirotation was also observed in benzene and carbon tetrachloride, and therefore neither ionisation nor the formation of hydrates or compounds of the acetal class is essential for the occurrence of this phenomenon.

139. "The alkylation of galactose." By James Colquhoun Irvine and Adam Cameron.

The silver oxide method of alkylation, when applied to α -methylgalactoside, gives rise to tetramethyl α -methylgalactoside, a colourless, refractive liquid (b. p. 136—137°/11 mm., $[\alpha]_D^{20}$ of the pure liquid is +105.7°, and in aqueous solution $[\alpha]_D^{20}$ is +143.4°). Hydrolysis with hot dilute hydrochloric acid leads to the production of tetramethyl galactose, a colourless, refractive syrup (b. p. 172°/13 mm.). After distillation, the alkylated sugar displays multirotation, not only in water, but also in alcohol and benzene, the permanent values for these three solvents being +109.5°, 62.6°, 90.0° respectively. In other respects, also, the behaviour of the compound supports the view that it has an oxidic structure.

When the substance is either heated with methyl alcohol and hydrochloric acid or treated with silver oxide and methyl iodide, the stereoisomeric tetramethyl α - and β -methylgalactosides are produced, the latter method giving a large excess of the β -compound, whilst the former yields a greater proportion of the α -isomeride. The crystalline β -form (m. p. 44—45°) is much more readily hydrolysed than its isomeride, either by dilute acids or by emulsin.

140. "A method for the rapid ultimate analysis of certain organic compounds." By John Norman Collie.

The method consists in burning the substance in a known volume of oxygen, noticing any change in the volume of the gas, and then, by

absorbing the carbon dioxide produced, data sufficient for the calculation of the percentage amounts of carbon and hydrogen are obtained.

Only those substances can be estimated which are not appreciably volatile in a vacuum, and which contain only carbon and hydrogen or carbon, hydrogen, and oxygen. The time required for an analysis is only about an hour; the amount of substance used can be reduced to nearly one-tenth of that ordinarily employed, and as the measurements depend on volumes of gases the method is very accurate.

141. "The comparative nitrifying power of soils." By Sydney Francis Ashby.

The method devised for comparing quantitatively the power of cultivated soils to convert their ammonia into nitrites and nitrates has justified itself by:—

(1) Yielding samples giving reasonably similar nitrifying power from different parts of the same field.

(2) Causing equal seedings from the same sample to show similar nitrifying power.

(3) Minimising loss of nitrogen by volatilisation of ammonia and denitrification during incubation.

(4) Limiting the incubation period to about 30 days.

(5) Showing a nitrifying power of the soils tested which corresponds with their fertility as gauged from manuring and crop production.

142. "The action of organic bases on olefinic ketonic compounds." By Siegfried Ruhemann and Edwin Roy Watson.

Benzylideneacetylacetone readily unites with *m*-toluidine, *p*-toluidine, *m*-chloroaniline, *p*-chloroaniline, β -naphthylamine, and piperidine, but it does not combine with *o*-toluidine, α -naphthylamine, or tetrahydroquinoline.

Piperidinobenzylacetylacetone, $C_6H_5 \cdot CH(NC_5H_{10}) \cdot CH(CO \cdot CH_3)_2$, is stable in a dry atmosphere, but in the presence of moisture it gradually decomposes with the formation of benzylidenebisacetylacetone, benzaldehyde, and piperidine.

The production of benzylidenebisacetylacetone and similar compounds from benzaldehyde and ketonic compounds is therefore preceded by the formation of additive compounds of piperidine with olefinic ketonic compounds. This view is supported by the fact that benzylideneacetylacetone, which combines with piperidine, also condenses with acetylacetone in the presence of the base to form benzylidenebisacetylacetone, whilst no such reaction takes place if tetrahydroquinoline, which does not form an additive compound with the olefinic ketone, is used instead of piperidine.

With phenylhydrazine, dibenzylideneacetone forms the phenylhydrazone, $(C_6H_5CH:CH)_2C:N\cdot NH\cdot C_6H_5$, and not an additive compound; with ammonia, it yields a mixture of substances from which has been isolated the compound having the formula $C_{34}H_{35}N_3$.

Benzylideneacetophenone dibromide, when condensed with ammonia, yields aminobenzylideneacetophenone, $C_6H_5\cdot C(NH_2):CH\cdot CO\cdot C_6H_5$, it therefore follows that the corresponding compound obtained by Wieland (*Ber.*, 1894, 27, 1150) from ammonia and *p*-nitrobenzylideneacetophenone dibromide is also unimolecular.

143. "Halides of the acridines and naphthacridines." By Alfred Senior and Percy Corlett Austin.

The halogens combine directly with the acridines, forming a series of well-defined, crystalline compounds, which are sparingly soluble in organic media, and are obtained by mixing the reagents either alone or in a suitable solvent. The products, which have characteristic colours, are unstable, especially in presence of water. The fluorescence, when in solution, which is so marked a character of acridines generally, and which depends on the presence of the acridine "fluorophore," is absent, except in three instances.

That these compounds are not substitution derivatives follows from their instability, the small number of halogen atoms which they contain, and the fact that no acridone is formed when they are treated with water or alkalis. They are therefore additive compounds, namely, halides. Moreover, the addition takes place in the acridine ring, for, were it otherwise, monadic atoms would be added only in pairs, which, however, is not the case, and a higher number would combine owing to the disruption of the centric benzene linkings.

Adopting this view, two formulæ are possible for the dihalides. The first, which is of the type of the dihydrides or dihydroacridines (Berthsen and Bender, *Ber.*, 1883, 18, 1802), is suggested for the non-fluorescent dihalides, and the second, corresponding with the acridinium salts, alkylhalides, and alkylhydroxides, is employed for the dihalides which exhibit fluorescence. In accordance with the foregoing hypothesis, the tetrahalides should have formulæ of the former non-fluorescent type, and acridine tetrabromide, the only tetrahalide described, was found to be non-fluorescent.

Those compounds which contain one halogen atom combined with one and three molecular proportions of base respectively are regarded as being products intermediate between the bases and the dihalides, in the one case, and the dihalides and tetrahalides in the other, and to these products dimolecular formulæ are assigned.

144. "Reactions involving the addition of hydrogen cyanide to carbon compounds. Part II. Cyanohydrins regarded as complex acids." By Arthur Lapworth.

Under certain conditions, an aqueous solution of potassium cyanide readily dissolves benzaldehyde and camphorquinone. From the resulting liquids, crystalline additive products having approximately the compositions $C_7H_6O, KCN, 2\frac{1}{2}H_2O$ and $C_{10}H_{14}O_2, KCN, 3H_2O$ have been isolated. These substances behave as salts of the corresponding cyanohydrins, which are probably much feebler acids than hydrocyanic acid itself.

145. "Reactions involving the addition of hydrogen cyanide to carbon compounds. Part III. Action of potassium cyanide on mesityl oxide." By Arthur Lapworth.

It was shown that when mesityl oxide is heated with potassium cyanide dissolved in dilute alcohol, hydrogen cyanide is first assumed at the ethylenic carbon linking, and that the potassium hydroxide which is simultaneously produced converts the product into mesitonic acid; more prolonged heating results in the formation of mesitylic acid, which necessitates the addition of a second molecule of hydrogen cyanide in this case to the carbonyl group, and the subsequent hydrolysis of the product.

146. "6-Aminocoumarin." By Gilbert Thomas Morgan and Frances Mary Gore Micklethwait.

6-Aminocoumarin, although resembling the naphthylamines in containing two unsaturated rings, nevertheless behaves towards diazonium salts like a para-substituted benzenoid amine, giving rise to stable diazoamino-derivatives.

This base and its mono- and di-alkylated compounds and the corresponding hydrazine and diazocyanide are all coloured substances, whereas the salts of these bases, the acyl derivatives of the primary and secondary amines, the nitrosoamines of the monoalkyl derivatives, the diazonium salts of the parent base and its quaternary bromides and iodides are colourless.

147. "Studies in asymmetric synthesis. I. Reduction of menthyl benzoylformate. II. Action of magnesium alkyl haloids on menthyl benzoylformate." By Alexander McKenzie.

When *l*-menthyl *dl*-mandelate is hydrolysed by an amount of potassium hydroxide insufficient for complete hydrolysis, an optically active mandelic acid is invariably obtained from the potassium salt thus formed. The mixture of esters remaining after this partial hydrolysis, when completely hydrolysed, yields mandelic acid which is either optically active or inactive, according to the experimental conditions. In the complete hydrolysis, by potassium hydroxide, of a mixture of *l*-menthyl *d*-mandelate and *l*-menthyl *l*-mandelate containing an excess of either of those esters, racemisation phenomena are observed.

On reducing menthyl benzoylformate to menthyl mandelate and hydrolysing the latter, the mandelic acid obtained was inactive. But it does not follow from this result that equal amounts of *l*-menthyl *d*-mandelate and *l*-menthyl *l*-mandelate were present in the product obtained by the reduction of menthyl benzoylformate, since, even if unequal amounts had been present, the mandelic acid obtained might still have been inactive owing to the racemising effect of the hydrolysing alkali.

Further investigation showed that a slight excess of *l*-menthyl *l*-mandelate was present in the reduction product, which, however, on hydrolysis, yielded *r*-mandelic acid.

When menthyl benzoylformate, $\text{PhCO}\cdot\text{CO}_2\cdot\text{C}_{10}\text{H}_{19}$, is acted on by magnesium methyl iodide and the magnesium addition compound then decomposed by water and dilute acid, a new asymmetric carbon atom is produced. In this instance, no racemising effects are observed on hydrolysing the product with alkali, since an optically active potassium salt is present in solution after the complete removal of the *l*-menthol, and this salt yields an optically active phenylmethylglycollic acid, $\text{CMePh(OH)}\cdot\text{CO}_2\text{H}$. An optically active phenylethylglycollic acid was also obtained in a similar manner.

That the optical activity exhibited by phenylmethylglycollic and phenylethylglycollic acids, prepared by Grignard's reaction, was actually due to their asymmetric synthesis was shown by preparing diphenylglycollic (benzilic) acid from menthyl benzoylformate and magnesium phenyl bromide. In this case, where a new asymmetric carbon atom was not produced, the resulting acid was inactive.

148. "The relation of position isomerism to optical activity. II. The rotation of the menthyl esters of the isomeric chlorobromobenzoic acids." By Julius Berend Cohen and Henry Stanley Raper.

The authors have extended the research of Briggs and Cohen on the relation of position isomerism to the rotations of the menthyl esters of the six dichlorobenzoic acids (*Trans.*, 1903, 83, 1213) by preparing and examining the menthyl esters of the ten isomeric chlorobromobenzoic acids.

The molecular rotations of these esters agree in a very satisfactory way with those of the dichlorobenzoic esters.

The greatest effect in decreasing the rotation is produced when the halogen enters the ortho-position with respect to the ester group; the least when both halogens are in the meta-position. The mean order of magnitude, beginning with the ester of lowest rotation, is as follows:

2:6; 2:3; 2:5; 2:4; 3:4; 3:5; phenyl,

which is precisely the order of rotation of the dichloro-esters.

When the chlorine is nearer to the ester group than the bromine, a greater depression in the rotation is produced than by the reverse arrangement. Moreover, when the chlorine occupies the ortho-position to the ester group, the rotation is lower than that of the corresponding dichloro-ester. The general effect of bromine is to influence the rotation less than the chlorine—a result which seems to follow from the effect of the monohalogen esters.

The great contrast afforded by the two symmetrical compounds of both series, namely, the 3:5- and 2:6-esters, is not a little remarkable, and these isomerides may be regarded as the first and last terms of a series in which the 2:6-compounds have a high melting point and low rotation, whilst the 3:5-isomerides have a low melting-point, low density, and high rotation.

149. "The relation of position isomerism to optical activity. III. The rotation of the menthyl esters of the isomeric iodobenzoic acids." By Julius Berend Cohen and Henry Stanley Raper.

In a former communication (Cohen and Briggs, *Trans.*, 1903, 83, 1216), the rotations of the menthyl esters of the three monochlorobenzoic acids were given and compared with the constants obtained for the monobromobenzoic esters by Tschugaeff. The authors have now determined the constants for the menthyl esters of the three iodobenzoic acids.

50. "The chlorination of the trichlorotoluenes in presence of the aluminium-mercury couple. The constitution of the tetrachlorotoluenes. Part V." By Julius Berend Cohen and Henry Drysdale Dakin.

In previous papers (Part III., *Trans.*, 1901, 79, 1111; Part IV., *Trans.*, 1902, 81, 1325), the authors have traced the progressive chlorination of toluene as far as the formation of the trichlorotoluenes. The products formed on introducing a fourth chlorine atom into each of the six trichlorotoluenes have now been investigated.

On chlorinating 3 : 4 : 5-trichlorotoluene at 0°, the chlorine enters the side-chain instead of the nucleus.

Although there appears to be no general law determining the position of the fourth entrant chlorine atom, yet there exists a remarkable agreement between the positions taken by the entrant chlorine atoms and nitro-groups when the first two chlorine atoms have been introduced into either benzene or toluene. Whatever the ultimate explanation may be, it is clear that after the first two chlorine atoms have been introduced into benzene and toluene the special rules which usually govern substitution are wholly or in part set aside in favour of a more general law which includes both the substituent chlorine atom and also the nitro-group.

151. "The chemical dynamics of the reactions between sodium thio-sulphate and organic halogen compounds. Part I. Alkyl haloids." By Arthur Slator.

The reactions between sodium thiosulphate and methyl, ethyl, and ethylene haloids have been investigated in dilute solution and shown to be in most cases bimolecular, thus: $\text{CR}_3\text{I} + \text{S}_2\text{O}_3'' = \text{CR}_3\text{S}_2\text{O}_3' + \text{I}'$. Water was used as a solvent whenever possible, but in a few cases a mixture of this liquid and alcohol had to be employed.

The rate of reaction is approximately trebled for a rise of 10°. The velocity-coefficients may be used to compare the reactivities of these haloids. With two of the compounds ($\text{C}_2\text{H}_4\text{ICl}$, $\text{C}_2\text{H}_4\text{BrCl}$), the velocity of the reaction with excess of thiosulphate is independent of this excess and the reaction is therefore unimolecular. To explain this result, it is suggested that the haloids are capable of existing in two tautomeric forms, and that the measurable reaction represents the change of one form into the other.

152. "Note on methyl fluoride." By John Norman Collie.

Methyl fluoride under 2 mm. pressure, when contained in a vacuum tube having aluminium electrodes and subjected to the spark from an

induction coil, gives a bluish-green colour. The spectrum, however, rapidly changes, and the characteristic lines of hydrogen make their appearance. When sparked under the ordinary pressure, the gas is almost immediately decomposed in the following manner: $4\text{CH}_3\text{F} = 4\text{C} + 4\text{H}_2 + 2\text{H}_2\text{F}_2$. In glass tubes, a secondary change occurs; the silicon fluoride formed by the action of the hydrogen fluoride on the glass is reduced by the hydrogen, and silicon is deposited: $\text{SiF}_4 + 2\text{H}_2 = 2\text{H}_2\text{F}_2 + \text{Si}$.

153. "Acetylenic ketones." By Edwin Roy Watson.

The action of various bases on bromobenzylideneacetophenone, $\text{C}_6\text{H}_5\cdot\text{CBr}\cdot\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_5$, has been investigated in the hope that a molecule of hydrogen bromide might thereby be eliminated from this compound (compare Ruhemann and Watson, *Trans.*, 1904, 85, 457). The action of solid powdered potash gives rise to phenylacetylene, potassium benzoate, and potassium bromide.

The action of alcoholic ammonia gives rise to aminobenzylideneacetophenone, $\text{C}_6\text{H}_5\cdot\text{C}(\text{NH}_2)\cdot\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_5$, and by the action of piperidine two compounds, dipiperidinobenzylacetophenone and piperidinobenzylideneacetophenone, are produced. Strong bases replace the bromine atom in bromobenzylideneacetophenone by an amino- or substituted amino-group.

Phenylpropiolyl chloride reacts readily with anisole to produce the expected acetylenic ketone, methoxybenzoylphenylacetylene. On substituting benzene for anisole the simple reaction no longer occurs, but several substances are produced, including a hydrocarbon having the empirical formula $\text{C}_{14}\text{H}_{12}$.

Methoxybenzoylphenylacetylene and piperidine yield piperidinomethoxybenzoylstyrene, $\text{C}_6\text{H}_5\cdot\text{C}(\text{NC}_5\text{H}_{10})\cdot\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_3$, whilst the action of hydroxylamine gives rise to 1-phenyl-3-methoxyphenylisooxazole.

Benzoylphenylacetylene yields the phenylhydrazone,



and the anilino benzoylstyrene, $\text{C}_6\text{H}_5\cdot\text{C}(\text{NH}\cdot\text{C}_6\text{H}_5)\cdot\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_5$, when treated with phenylhydrazine and aniline respectively.

154. "Note on bergamot oil and other oils of the citrus series." By Herbert Edward Burgess and Theodore Henry Page.

Acetic acid, octylene, pinene, camphene, and limene have been identified as constituents of a specimen of pure oil of bergamot. The pungency of the first fractions of this oil on distillation is accounted

for by the acetic acid, which was also found in smaller quantities in lemon oil and is probably present in the other oils of this series.

The octylene found in lemon oil was identical with that in bergamot oil, for both gave butyric acid on oxidation with potassium permanganate. It is probably a normal constituent of the citrus oils. A second phenylurethane isolated from the terpeneol fraction of distilled oil of limes melts at 132° , is more soluble than that obtained from ordinary terpeneol, crystallises in tufts of needles, and gives on hydrolysis an oil with an intense odour of distilled oil of limes.

155. "The resolution of externally compensated dihydro- α -methylindole." By William Jackson Pope and George Clarke, jun.

On crystallising externally compensated dihydro- α -methylindole with *d*-bromocamphorsulphonic acid, *l*-dihydro- α -methylindole *d*-bromocamphorsulphonate, $C_9H_{11}N, C_{10}H_{14}BrO \cdot SO_3H$, first separates, and on purification crystallises in needles (m. p. $179.5-180.5^{\circ}$; $[M]_D + 278^{\circ}$ in aqueous solution). With caustic soda, it yields *l*-dihydro- α -methylindole, which is obtained as a colourless oil (b. p. $228-229^{\circ}$; $[a]_D - 13.61^{\circ}$ in a 1 dem. tube). The base is dextrorotatory in ethyl alcohol and benzene solutions, but lævorotatory in ethereal solution.

A more sparingly soluble dihydro- α -methylindole *d*-bromocamphorsulphonate (m. p. $124-125^{\circ}$) accompanies the above salt, but, although it has the low molecular rotatory power of $[M]_D + 242.6^{\circ}$ in aqueous solution, corresponding with the presence of a basic ion of $[M]_D - 30^{\circ}$, this salt yields inactive base and inactive benzoyl and acetyl derivatives.

On adding caustic soda to the final mother liquors obtained during the resolution, impure *d*-dihydro- α -methylindole separates, but was not obtained free from the lævo-isomeride; its benzoyl and acetyl derivatives were, however, prepared in a state of purity, and have properties corresponding with those of their optical antipodes.

156. "The vapour pressures of sulphuric acid solutions and the molecular condition of sulphuric acid in concentrated solution." By Bryce Chudleigh Burt.

The vapour pressures of sulphuric acid solutions of various concentrations (from 25 to 95 per cent. H_2SO_4) have been determined by an ebullioscopic method. The values so obtained lie on smooth curves when plotted against temperature and concentration. The molecular weight has been calculated from Raoult's corrected formula :

$$m = M \cdot \frac{g}{G} \cdot \frac{p'}{p - p'}$$

where m = molecular weight of solute; M = molecular weight of solvent in the gaseous state; g = weight of solute; G = weight of solvent; p = vapour pressure of pure solvent; p' = vapour pressure of solution. The values for m obtained vary over very wide limits, increasing with rise of temperature and decreasing with increase in concentration. The different values do not lie on smooth curves when plotted against temperature and concentration.

These abnormalities can only be explained by supposing that combination occurs between the solvent and solute with the formation of complex molecules, the formation of such complexes being favoured by an increase in concentration but not by a rise in temperature.

157. "Reactions involving the addition of hydrogen cyanide to carbon compounds. Part IV. Addition of hydrogen cyanide to benzylideneacetophenone." By Archie Cecil Osborn Hann and Arthur Lapworth.

The addition of hydrogen cyanide to benzylideneacetophenone takes place only in presence of a considerable quantity of potassium cyanide, and the failure of Rupe and Schneide (*Ber.*, 1895, **28**, 957) to bring about the addition process is thus explained. When the solution is but feebly alkaline, the product is β -benzoyl- α -phenylpropionitrile, $\text{CHPh}(\text{CN})\cdot\text{CH}_2\cdot\text{COPh}$, but in presence of alkali the latter condenses with unaltered benzylideneacetophenone to yield the compound $\text{C}_{31}\text{H}_{23}\text{ON}$, which Rupe and Schneide obtained in small quantities.

The *oxime*, $\text{CHPh}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CPh}\cdot\text{N}\cdot\text{OH}$, when warmed with sulphuric acid, undergoes the Beckmann change, yielding phenylsuccinic acid and aniline, by which reaction the constitution of the ketonic acid is established.

By means of the quinine salt, β -benzoyl- α -phenylpropionic acid was resolved into its optical isomerides; the *laevo*-acid, melting at 176 — 178° in 6 per cent. ethyl acetate solution, had $[\alpha]_D - 157.57^\circ$, whilst the *dextro*-acid had $[\alpha]_D + 157.3^\circ$.

158. "The bromination of silver cyanate." By George Dean.

Silver cyanate, when treated with an equivalent weight of bromine in a sealed tube, yielded a yellow product, AgCNOBr . The substance, which did not darken on exposure to light, gave off bromine when heated above 70° . At 300 — 400° , the bromine evolved from the substance was accompanied by a thick sublimate of cyanogen bromide. The substance dissociated under 10 — 20 mm. pressure. Water acts on the compound, yielding silver bromide, cyanuric acid, carbon dioxide, and nitrogen; hydrochloric acid gives rise to a mixture of silver chloride

and bromide, whilst cyanogen chloride, bromine, and oxygen are eliminated. The compound oxidises alcohol to acetaldehyde. When the cyanate was brominated at a lower temperature, much more halogen was absorbed; the product, however, was readily decomposed a current of air, leaving the less brominated compound.

159. "The decomposition of chloral hydrate by sodium hydroxide and by certain salts." Emil Alphonse Werner.

It is shown that the quantity of chloral hydrate decomposed by sodium hydroxide is a function of the temperature, for one molecular proportion of this alkali is capable of decomposing from one to four molecular proportions of the hydrate with production of chloroform, sodium formate, and free formic acid. Sodium acetate and similar salts are also capable of decomposing the hydrate with the production of formic acid. Water and dilute acids do not decompose chloral hydrate in this manner.

Two alternative theories are put forward to explain the decomposition. Firstly, it is assumed that a sodium derivative, $\text{CCl}_3 \cdot \text{CH}(\text{ONa}) \cdot \text{OH}$, formed on adding the alkali or salt, is immediately decomposed into chloroform and sodium formate. The decomposition of relatively large proportions of the hydrate by sodium hydroxide is easily explained in this way.

Secondly, the production of "nascent" carbon monoxide, $>\text{C}:\text{O}$, as distinct from ClO , is suggested, this hypothetical substance then uniting with water to give formic acid.

160. "Contributions to the history of glyoxylic acid." By Heinrich Debus.

Two views still prevail with regard to the formula of glyoxylic acid: some chemists represent its composition by the formula $\text{C}_2\text{H}_2\text{O}_3, \text{H}_2\text{O}$, whilst others prefer the expression $\text{C}_2\text{H}_4\text{O}_4$. The author, after discussing the arguments in favour of each formula, comes to the conclusion that the formula $\text{C}_2\text{H}_2\text{O}_3, \text{H}_2\text{O}$ is more in harmony with the properties of glyoxylic acid than the other.

Some basic salts of glyoxylic acid are described which readily decompose into the corresponding glycollates and oxalates.

161. "The colouring matters of the stilbene group. I." By Arthur George Green.

The colouring matters of the stilbene class cannot have the simple structure assigned to them either by O. Fischer and Hepp or by Bender

and Schultz. Apart from the general improbability that substances so constituted would have dyeing properties, the following facts indicate that they have a more complex structure:—

(1) Colouring matters can be obtained from *p*-nitrotoluenesulphonic acid by condensation with alkalis under suitable conditions, which, although having the general characteristics of Curcumine S or Direct Yellow, contain aldehydic groups in addition to the stilbene group.

(2) Stilbene dyes of mixed type can be obtained by condensing dinitrostilbenedisulphonic acid with aromatic amines under the influence of alkalis.

(3) Curcumine or Direct Yellow does not give rise on oxidation to dinitrostilbenedisulphonic acid, but furnishes a yellow dye of greener shade which is very similar to the first product of the alkaline reduction of dinitrostilbenedisulphonic acid.

The author has endeavoured to elucidate the constitution of the crimson-red compound which invariably precedes the formation of the stilbene colouring matter and is evidently the first phase of the condensation. The fact that this substance, on oxidation with hypochlorite, gives dinitrostilbenedisulphonic acid (Green and Wahl, *Ber.*, 1897, 30, 3097) and is again regenerated from this acid on reduction, supported by a study of its phenyl ester and the analogous chloro-compound (compare next abstract), leads to the view that the crimson-red intermediate compound is a nitroso-stilbene or stilbene nitrolic acid having a quinonoid structure in alkaline solution.

162. "The colouring matters of the stilbene group. II." By Arthur George Green, Fred Scholefield, and Fred Marsden.

In order to elucidate the constitution of the crimson-red compound obtained on heating *p*-nitrotoluenesulphonic acid with caustic alkalis, and which forms the first phase of the stilbene condensation, the authors have investigated the behaviour of the corresponding phenyl ester, $C_6H_3(CH_3)(SO_3C_6H_5)(NO_2)[1:2:4]$, and chloro-compound, $C_6H_3(CH_3)Cl(NO_2)[1:2:4]$. The first of these compounds, in alcoholic solution, gives, on adding caustic soda, an intense bright blue coloration even in the cold; the second gives a reddish-violet coloration at 20—30°.

It being found impracticable to isolate these coloured substances on account of their extreme instability, their behaviour on oxidation was studied. They are rapidly decolorised both by sodium hypochlorite and by air, and give rise to derivatives of dinitrostilbene. From the phenyl ester, a mixture of the *trans*- and *cis*-phenyl dinitrostilbenedisulphonates was produced. The same two compounds were also obtained from Green and Wahl's dinitrostilbenedisulphonic acid by conversion

into the sulphonic chloride and treatment with sodium phenoxide. This fact serves to confirm the constitution assigned above, and also shows that the dinitrostilbenedisulphonic acid, and probably also the crimson-red intermediate compound and the stilbene colouring matters generally, must consist of mixtures of *trans*- and *cis*-isomerides.

The reddish-violet intermediate compound from *o*-chloro-*p*-nitrotoluene, on oxidation with air or sodium hypochlorite, yielded a mixture of *trans*- and *cis*-dichlorodinitrostilbenes; the yield of the two isomerides being nearly theoretical, the formation of a third substance is excluded and a simple connection between the coloured intermediate compound and the respective dinitrostilbene derivative is indicated. This is further supported by the fact that these dinitrostilbene derivatives are readily reconverted by alkaline reducing agents, such as phenylhydrazine and caustic soda, into the blue and reddish-violet compounds from which they are obtained. The authors are thus led to assign to the latter the structure of nitrosostilbenes or stilbene nitrolic acids.

163. "Researches on chromorganic acids: the behaviour of chromic hydroxide towards oxalic acid and certain other organic acids."

By Emil Alphonse Werner.

An aqueous solution of oxalic acid, when saturated with chromic hydroxide, yields a deep purplish-red liquid, which, on evaporation, leaves a dark green residue, appearing almost black by reflected light. This compound has the properties of a true chromoxalic acid, $\text{H}_5\text{Cr}_4(\text{C}_2\text{O}_4)_6(\text{OH})_5 \cdot 4\text{H}_2\text{O}$, and yields an ammonium salt, $(\text{NH}_4)_5\text{Cr}_4(\text{C}_2\text{O}_4)_6(\text{OH})_5 \cdot 2\text{H}_2\text{O}$.

Whilst thoroughly washed chromic hydroxide is readily dissolved by oxalic acid in the proportion required by the formula $\text{Cr}_2(\text{C}_2\text{O}_4)_3$, this is not the case with other related organic acids. Under similar conditions, malonic acid dissolves approximately 50 per cent. of the calculated amount, whereas, with succinic acid, the interaction is inappreciable. A chromomalonic acid, having the formula $\text{H}_5\text{Cr}_4(\text{C}_3\text{H}_2\text{O}_4)_6(\text{OH})_5 \cdot 6\text{H}_2\text{O}$, analogous to the chromoxalic acid, was obtained, and also a chromomalonate, $\text{K}_2\text{Cr}_2(\text{C}_3\text{H}_2\text{O}_4)_4 \cdot 10\text{H}_2\text{O}$, forming dark purplish-red crystals, the analogue of Croft's red chromoxalate.

The proportion of chromic hydroxide dissolved by malic, tartaric, tricarballic, citric, glycollic, and lactic acids under the conditions described is relatively small, varying from a minimum of 12 per cent. (malic acid) to a maximum of 27 per cent. (lactic acid). In all these cases, chromorganic acids are produced, having, in general, properties resembling those of chromoxalic acid. With tartaric acid, a saline chromium tartrate, $\text{Cr}_2(\text{C}_4\text{H}_4\text{O}_6)_3$, is also formed. When the red salt, $\text{K}_2\text{Cr}_2(\text{C}_2\text{O}_4)_4 \cdot 10\text{H}_2\text{O}$, is boiled in aqueous solution with 2 mols. of

potassium oxalate, the blue chromoxalate, $K_6Cr_2(C_2O_4)_6 \cdot 6H_2O$, is produced; a similar result is brought about by other salts, such as potassium acetate, malonate, or succinate, and so far no chromium compound containing two different acid groups has been obtained.

A well-defined potassium boro-oxalate, $K_2(Bo)_2(C_2O_4)_3 \cdot 3H_2O$, which is readily obtained by boiling solutions of potassium metaborate and oxalic acid or boric acid and potassium hydrogen oxalate is described. A similar compound is not formed with malonic or succinic acid.

164. "The effect of colloidal platinum on mixtures of Caro's persulphuric acid with hydrogen peroxide." By Thomas Slater Price and John Albert Newton Friend.

Although solutions of hydrogen peroxide and Caro's acid have no appreciable action on each other, the addition of colloidal platinum causes interaction, oxygen being evolved, according to the equation $H_2SO_5 + H_2O_2 = H_2SO_4 + H_2O + O_2$, or $H_2S_2O_9 + 2H_2O_2 = 2H_2SO_4 + H_2O + 2O_2$. The rate of evolution of oxygen gives a measure of the velocity of the reaction; titration methods cannot be used, since there are no accurate methods of estimating hydrogen peroxide and Caro's acid in the presence of each other. It was found that, as long as the platinum was not precipitated out of the solution, the velocity constants, whether of the second or the third order (corresponding with the above equations), continually increased. This increase is considered to be due to two causes: (1) the gradual increase in the reactivity of the platinum during the reaction; (2) the independent and concurrent decomposition of the hydrogen peroxide and Caro's acid respectively. In some cases, the velocity curve was a straight line.

The effect of varying the concentration of the platinum was also studied, but no definite connection between concentration and velocity could be traced, except that a diminution in velocity was associated with a decrease in concentration of the platinum. In alkaline solutions, the results obtained were indefinite, since interaction takes place in the absence of platinum and the velocity seems to depend on the rate of stirring.

165. "The acylation of amides." By Arthur Walsh Titherley.

The conversion of a primary into a secondary amide and a secondary into a tertiary amide cannot, in general, be effected by treatment with acyl chlorides and anhydrides, but by first replacing the hydrogen of the $-CO \cdot NH_2$ or $-CO \cdot NH \cdot CO-$ group by sodium; the resulting sodium acylamide reacts usually with considerable energy with acyl chlorides

or, preferably, anhydrides, yielding acylated derivatives. Sodium benzamide and benzoic anhydride, for example, yield sodium dibenzamide and benzoate. At the same time, a tertiary amide (tribenzamide) is formed owing to the interaction of a portion of the sodium dibenzamide and benzoic anhydride.

Although the action is normal in the aromatic and aliphatic series respectively, abnormal results are obtained on attempting to apply the method to the synthesis of mixed aliphatic aromatic secondary amides. Thus, neither sodium acetamide and benzoic anhydride nor sodium benzamide and acetic anhydride yield the expected acetylbenzamide in appreciable quantity, the main product of either of these condensations being sodium dibenzamide.

Cyclic anhydrides appear to behave normally. Thus, succinic anhydride and sodium benzamide give rise to *benzoylsuccinamic acid* (needles, m. p. 180°) and *s-dibenzoylsuccinamide* (m. p. 211°).

A further application of sodium acylamides for the purpose of acylation is based on their condensation with esters (*Trans.*, 1902, 81, 1520), but the condensation is abnormal with esters and sodium acylamides which contain the groups $-\text{CH}_2\cdot\text{CO}_2\text{Et}$ and $-\text{CH}_2\cdot\text{CO}\cdot\text{NHNa}$ respectively. Methyl oxalate yields the disodium derivative of dibenzoyloxamide, but benzoyloxalimide, which was also anticipated, is not produced.

s-Dibenzoyloxamide (m. p. 227°) is readily soluble in sodium hydroxide, but the solution readily undergoes hydrolysis, forming benzamide and sodium oxalate. Ethyl succinate and sodium benzamide readily react, but do not yield either ethyl benzoyl succinamate, dibenzoylsuccinamide, or benzoylsuccinimide; the chief products are sodium succinimide and ethyl benzoate.

A very convenient process for acylating amides direct consists in treating directly with the acyl chloride the amide dissolved in pyridine (compare Freundler, *Compt. rend.*, 1902, 136, 1553; 1903, 137, 712—714). The method is limited in the same sense as the sodium acylamide anhydride method, since in this case also aromatic acyl radicles tend to displace aliphatic groups; hence it is impossible to prepare acetylbenzamide from benzoyl chloride and a pyridine solution of acetamide. That the method may be applied to the acylation of secondary as well as primary amides is shown by the fact that dibenzamide when subjected to this process yields 50 per cent. of tribenzamide.

Benzoylsuccinimide (m. p. $129-130^{\circ}$) is readily obtained by the action of benzoyl chloride on a pyridine solution of succinimide.

166. "The composition of beryl." By James Holms Pollok.

The irregular results obtained on the analysis of compounds of glucina, prepared from various samples of the oxide, suggested that there was something in the composition of the beryl that had so far been overlooked.

The glucina employed was extracted from Limoges beryl during a previous research, and was known to give too high an equivalent, although analysis failed to indicate the presence of aluminium or any other base. This glucina was fractionated by crystallisation of the sulphate, by solution in ammonium carbonate, and by precipitation from hydrofluoric acid solution by potassium hydrogen fluoride. The glucina was recovered from the various fractions, converted into anhydrous chloride, and the various specimens of this salt analysed. In certain fractions, a progressive rise in the equivalent of the base was observed, giving figures ranging from 4.77 to 8.17.

Samples of glucinum chloride were then fractionated by distillation, the most volatile and least volatile portions being analysed separately. Three samples of the most volatile portions yielded equivalents of 9.08, 10.81, and 11.29.

Other fractions obtained by collecting the chloride that was first formed, apart from that which distilled over later, gave, on analysis, equivalents of 12.30, 14.80, and 18.74.

Only a small quantity of the chloride with the highest equivalent was obtained; the most careful analysis failed to detect in it the presence of aluminium, iron, or any other element, the sample having the chemical properties of glucinum only.

A spectroscopic examination of the various specimens with high equivalents showed that certain lines, only faintly visible in ordinary samples of glucina, became steadily stronger as the equivalent increased, and the known lines of glucinum became somewhat fainter.

These results indicate that beryl contains a new element having in the main the chemical properties of glucinum, but a much higher equivalent; its chloride is more volatile and more readily formed than that of glucinum, and the oxide is not so readily precipitated from a hydrofluoric acid solution by potassium hydrogen fluoride.

Thursday, November 3rd, 1904. Prof. W. A. TILDEN, D.Sc., F.R.S., President, in the Chair.

Messrs. C. R. Beck, J. H. Johnston, R. Lessing, J. Marsh, and H. S. Shelton were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs.

Walter Henry Bentley, B.A., 18, Oaten Hill, Canterbury.

John Wyclif Black, 20, Mardale Crescent, Edinburgh.

Thomas Story Busher, B.A., Queen's College, Oxford.

Lawrence Caldecott, 47, Woburn Place, Russell Square, W.C.

Robert John Caldwell, B.Sc., A.C.G.I., 49, Merritt Road, Crofton Park, S.E.

Peter Skinner Clark, M.B., Ch.M., Cape Town, Cape Colony, South Africa.

Frederick Clarkson-Harold, 10, Fee's Terrace, Longford, Ireland.

Robert Cornthwaite, Agricultural Laboratory, Halifax.

William Crabb, B.Sc., The Grammar School, Penistone, Yorks.

James Edward Cunningham, A.R.C.S., 21, Blenheim Gardens, Willesden Green, N.W.

Harold Deane, B.Sc., 34, Drakefield Road, Upper Tooting, S.W.

Francis Dickinson, 26, O'Connell Avenue, Berkeley Road, Dublin.

Edward Evans, 33, Ranelagh Road, Westminster, S.W.

Thomas Wallace Fagan, B.A., Harper Adams Agricultural College, Newport, Salop.

John Kerr Forrest, Hawsleigh, Balaclava Road, St. Kilda, N.S.W.

Thomas Reginald Hodgson, The Sycamores, Poulton-le-Fylde, Lancs.

George William Thomas Horrod, 294, Brixton Hill, S.W.

John Kenneth Harold Inglis, M.A., B.Sc., University College, W.C.

Thomas Campbell James, B.A., B.Sc., 4, Belmont Terrace, Llanelly.

Walter Richmond James, 49, Wednesfield Road, Wolverhampton.

John Richard Johnson, Apothecaries' Hall, E.C.

Horace Francis Jones, 3, Kerry Crescent, Calne, Wilts.

William App Jones, A.B., A.M., Ph.D., 12E, 18th Street, New York.

Alfred Francis Joseph, A.R.C.S., 95, Marylands Road, Maida Vale, W.

James Stanley Lauder, c/o B. Harvey, Qu'Appelle, N.W.T., Assa, Canada.

Arthur Garfield Levy, B.Sc., A.I.C., c/o B. Blount, Esq., 76, York Street, S.W.

James Patrick Longstaff, B.Sc., 19, Fettes Row, Edinburgh.

Arthur Thomas McDougall, B.A., 3, Albion Road, College Park, S.E.

Harold Joseph Clarke Mathews, Massey's Brewery, Ltd., Burnley, Lancs.

Ernest Westby Millar, A.R.C.S., Windsor, Monkstown, Co. Dublin.
 Marie Jean Louis Ernest Rouillard, B.Sc., Malvern, Natal.
 Percy Edwin Spielmann, A.R.C.S., 21, Cadogan Gardens, S.W.
 Harry Stanley, B.Sc., The Park, Southend Village, Catford, S.E.
 Thomas Sutcliffe, 19, Rhodes Street, Halifax, Yorks.
 Paul John Thibault, Howell, N.S.W.
 Douglas Frank Twiss, M.Sc., 89, Wood Lane, Harborne, Birmingham.
 Herbert Wood Watson, B.Sc., 111, Brudenell Road, Hyde Park, Leeds.
 William Henry Willcox, M.D., B.Sc., F.I.C., St. Mary's Hospital, W.
 Frank John Wyeth, M.A., 14, Preston Drove, Brighton.

The PRESIDENT, in announcing the lamented death of Professor Lobry de Bruyn, which occurred in July, after a short illness, reminded the Society that the deceased was one of the Honorary Foreign Members elected recently. A letter of sympathy and condolence had been immediately sent in the name of the Society to the widow, and it was hoped that an obituary notice would shortly appear in the Journal.

Of the following papers, those marked * were read :

***167. "Studies on the dynamic isomerism of α - and β -crotonic acids. Part I." By Robert Selby Morrell and Edward Kenneth Hanson.**

To show the change in the melting point with variation in the composition of a mixture of α - and β -crotonic acids at temperatures below the melting point of the less fusible component (α -crotonic acid), weighed quantities of the α -acid were added to a known weight of the β -acid, and the freezing point of the mixture observed. It was found that the freezing point of the β -crotonic acid fell from 14.96° to a minimum of -1.1° , and then rose to 43.9° on gradual addition of the α -acid until the mixture contained 30.8 per cent. of the β -acid. To complete the melting point curve, the lowering of the freezing point of α -crotonic acid by the β -isomeride was observed, and it was found that the curve was a continuous one from 15° through -3° (eutectic point) to 71.9° . There is no compound of α - and β -crotonic acids between these temperatures.

The investigation on the composition of the two acids at temperatures between 100° and 168° showed that β -crotonic acid changed on heating into the α -modification, and the composition of the mixture was found by cooling the fused mass rapidly and determining its freezing point. From the observed values of the freezing points for known mixtures of the two acids, the composition of the mixture was fixed

without having recourse to estimation by chemical methods. At 168° , the curve showing the transformation of the β -acid into the α -acid met the similar curve for the α -acid changing into the β -acid, the composition at this point was 76 and 24 per cent. of the α - and β -acids respectively. The boiling point under the ordinary pressure of a mixture of α - and β -crotonic acids is 168 — 174° (compare Michael, *J. pr. Chem.*, 1892, [ii], 46, 146).

These preliminary experiments furnish no evidence as to the existence of a compound of α - and β -crotonic acids between 100° and 168° .

***168. "The constitution of nitrogen iodide." By Oswald Silberrad.**

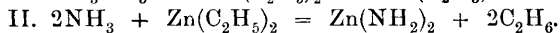
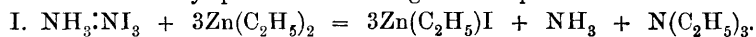
The empirical formula of nitrogen iodide has been established by Chattaway (*Amer. Chem. J.*, 1900, 23, 363, 369, and 1901, 24, 138, 159, 318, 330, 342) as $N_2H_3I_3$, but the analytical results obtained by earlier workers showed great variations, chiefly due to unsuitable methods of preparation, insufficient precautions against the decomposing action of light, and faulty methods of analysis. In view of the methods of preparation and properties of the compound, the formula $N_2H_3I_3$ admits of two possible constitutions: $NH_3 \cdot NI_3$ and $NHI_2 \cdot NH_2I$. Chattaway's work does not differentiate between these two formulæ, and the earlier investigations offer no further proof as to the constitution. On the one hand, the liberation of ammonia by the action of acids supports the former configuration, whilst the formation of di-iodomethylamine by the action of methyl iodide appears to render the latter formula probable.

No direct derivatives of nitrogen iodide have so far been prepared in a pure state, the metallic compounds investigated have been incorrectly formulated owing to impurities in the products, and the only organic derivatives of nitrogen iodide hitherto obtained are those prepared by Stahlschmidt (*Poggendorff's Ann.*, 1863, 119, 421) by the action of methyl iodide. These substances are so indirectly related to nitrogen iodide that they afford no definite proof as to its constitution.

In order to obtain substitution products closely related to nitrogen iodide, the action of zinc ethyl has been studied, and in this way it has been found possible to obtain direct proofs as to the constitution of the iodide.

Zinc ethyl reacts slowly with nitrogen iodide, producing volatile paraffins together with a white, amorphous compound, insoluble in ether, from which ammonia and triethylamine are obtained on treatment with dilute acid and subsequent distillation with aqueous

caustic potash. From this it is evident that the constitution of nitrogen iodide is represented by the formula $\text{NH}_3\cdot\text{NI}_3$, and that the action of zinc ethyl proceeds according to the equation :



This formula for the iodide is also supported by many of the observations of earlier investigators.

DISCUSSION.

Dr. CHATAWAY recalled the fact that in conjunction with Dr. Orton (*Amer. Chem. Journal*, 1901, 24, 342) he had shown that the formula $\text{H}_3\text{N}\cdot\text{NI}_3$ alone could explain the actions which take place when nitrogen iodide is slowly decomposed by a stream of water. In such a progressive decomposition, this molecule is broken up and the ammonia washed away, while NI_3 mixed with iodine remains in the solid residue. If the ratio $\text{N} : 3\text{I}$ could have been obtained, the formula would have been established beyond question, but, owing to the accumulation of iodine, a possibility of experimental error was introduced, and the ratio $1\cdot18\text{N} : 3\text{I}$ was the nearest approach to this on which they felt able to rely confidently ; this ratio, however, excludes all formulæ except the one they put forward. Although he regarded this formula as undoubtedly correct, nevertheless Dr. Silberrad's evidence was not quite conclusive. He drew attention to the small yield of triethylamine, and suggested that under the experimental conditions much of the base would be found in combination with ethyl iodide as tetraethylammonium iodide. It seemed unlikely that nitrogen iodide could be properly dried in quantity by washing with alcohol and afterwards with ether, especially as the compound so very readily interacted with alcohol with the production of ethyl iodide, aldehyde, and ammonia. The triethylamine obtained under these conditions might have been formed by the interaction of ethyl iodide and the liberated ammonia.

He hoped to be able shortly to publish the results obtained by the study of the interaction of nitrogen iodide and the magnesium alkyl compounds, particularly the benzyl derivatives.

Mr. SMART, in replying on behalf of Dr. Silberrad, who was absent, stated that, although ammonia was produced in quantitative yield by the interaction of nitrogen iodide and zinc ethyl, yet the proportion of triethylamine obtained in these experiments was so small that it could not be detected until the experimental conditions had been carefully worked out, and even then large quantities of the iodide had to be treated in order that the base might be isolated and identified. The personal risk involved in treating a kilogram of nitrogen iodide under ether with zinc ethyl was very small in comparison with the

danger incurred in dropping the dry iodide into an ethereal solution of zinc ethyl. He believed that a pure metallic derivative of the nitrogen iodide had actually been obtained, and that a paper on this subject would shortly be communicated to the Society.

***169. "The available plant food in soils." By Herbert Ingle.**

The results of the author's investigation of the available plant food in soils lead to the following conclusions :

(1) That extraction with a 1 per cent. solution of citric acid for 7 days renders a soil much less fertile, especially at first, but that chemical changes in such soil, during the growth of the plants, gradually render it again capable of supplying plant food.

(2) That beans are able to extract a larger portion of the potash and phosphoric acid present in the soil than barley. This was especially so in the case where extracted soil was used.

(3) That Dyer's method (*Trans.*, 1894, 65, 115) of determining "available" plant food in soils is of considerable value in estimating their relative fertility, but that another factor must be considered, namely, the rate at which the "available" plant food is renewed, especially if the soils exist under different climatic conditions.

Whilst this is probably the same or nearly so for soils under similar climatic conditions, it may be, and probably is, very different in tropical or sub-tropical soils to what it is in those of temperate climates.

DISCUSSION.

Dr. DYER said that he had seen photographs of Mr. Ingle's pot culture experiments, and these certainly seemed to confirm the view that the phosphoric acid and potash soluble in 1 per cent. citric acid solution corresponded with the quantity of those constituents immediately available as plant food. But the most interesting part of Mr. Ingle's work on the subject was that showing the recuperative power of soils even after they had been artificially denuded of immediately available mineral food.

170. "The basic properties of oxygen : compounds of the ethers with nitric acid." By Julius Berend Cohen and John Gatecliff.

In view of recently published results on the additive compounds of the ethers, the following observations which were made early in the year may be of interest. In extracting with ordinary ether the products of the nitric acid oxidation of substituted toluenes, it was

frequently observed that, after dehydrating and removing the ether on the water-bath, a small quantity of yellow liquid remained which had a characteristic odour quite unlike that of ether. If this liquid were more strongly heated, or even left for a time, it decomposed with a succession of little explosions and the evolution of nitrous fumes. The liquid is produced by the action of nitric acid on ether and behaves qualitatively like a mixture of these two substances. When added to strong sulphuric acid, nitric oxide is evolved, this result being also obtained by adding strong nitric acid to a mixture of strong sulphuric acid and ether. The liquid behaves like nitric acid to phenol, benzene, and aniline. In order to ascertain whether it had a definite composition the following experiments were made. Definite volumes of the purified ether and dilute nitric acid ($1\text{HNO}_3:2\text{H}_2\text{O}$) were shaken up in a separating funnel, the lower layer was removed, and the ethereal layer dehydrated for 24 hours over anhydrous sodium sulphate. The excess of ether was then removed by distillation until the thermometer registered 50° , when the process was stopped, for if the temperature rises above this point decomposition occurs and brown fumes are evolved. Air was now blown into the pale yellow residue contained in a beaker until the odour of ether had almost disappeared. As in this state the liquid decomposes rapidly at the ordinary temperature and slowly even at 0° , quantities of one to two grams were rapidly weighed and made up with water to 100 c.c. A measured volume was then titrated with standard caustic soda, using methyl-orange as indicator. The following results were obtained with purified methylated ether, ethyl ether, and propyl ether.

Ether employed.	Percentage of nitric acid in the product.	Volumes of ether and dilute nitric acid taken.			
Methylated ether ...	45.2	50 c.c.	HNO_3 :	50 c.c.	ether
„ ...	44.4*	50 „	„	50 „	„
„ ...	44.4	25 „	„	50 „	„
Ethyl ether	47.3	50 „	„	50 „	„
„	47.5	50 „	„	50 „	„
Propyl ether	33.8	50 „	„	50 „	„
„	35.9	50 „	„	50 „	„

* The ether in this case was not distilled, but evaporated at the ordinary temperature under 20 mm. pressure.

The calculated amounts of nitric acid corresponding with the formulæ $(\text{C}_2\text{H}_5)_2\text{O}, \text{HNO}_3$ and $(\text{C}_3\text{H}_7)_2\text{O}, \text{HNO}_3$ are 46 and 38.2 per cent. respectively. The agreement in the case of ethyl ether is quite satisfactory. The compound with propyl ether is evidently less stable at the ordinary temperature, the affinity for nitric acid appearing to diminish with increasing molecular weight. Amyl ether and dilute

nitric acid have no interaction at the ordinary temperature, and this is also the case with dimethylquinol, the only aromatic ether investigated.

171. "The condensation of formaldehyde with acetone. A preliminary note." By Emil Alphonse Werner.

When acetone is mixed with a 40 per cent. solution of formaldehyde, no interaction takes place until a small amount of alkali is added ; if the liquids are mixed in the undiluted form, the addition of a small amount of caustic potash causes after a few moments a very violent reaction, the liquid boils, and an orange-red, resinous condensation product separates.

When the substances are mixed in 10 per cent. aqueous solution, the reaction proceeds much more slowly, the liquid gradually assumes a dark yellow colour, showing a green fluorescence ; after one hour, the condensation product commences to separate as a bright orange-yellow powder, and at the end of 24 hours the reaction is complete. During the change, the alkalinity of the liquid diminishes considerably. The condensation product, when thoroughly washed and dried, forms an orange-yellow, amorphous, satiny powder with a peculiar odour. It has the empirical formula C_4H_6O : analysis gave $C = 68.97$ and 69.58 , $H = 7.46$ and 7.54 per cent., whilst the calculated percentages are $C = 69.56$, $H = 7.24$. The compound is freely soluble in alcohol, acetone, or glacial acetic acid, and is precipitated unchanged by water ; it dissolves sparingly in benzene, chloroform, or ether. The same substance is produced whether the acetone or the formaldehyde be used in excess.

It might have been expected that a compound having the composition C_4H_6O , that is, a polymeride of $CH:CH \cdot CO \cdot CH_3$ ($C = 68.56$, $H = 8.56$), would have been formed ; this, however, does not appear to be the case. With bromine in glacial acetic acid solution, it behaves as a saturated compound, hydrogen bromide is evolved, and a mono-brominated derivative formed, which separates on diluting with water as a dark brown powder.

The addition of hydrochloric acid to the alkaline filtrate from the original experiment produces a yellow precipitate having the same composition as the orange-yellow condensation product.

172. "The union of hydrogen and chlorine. Rate of decay of the activity of gaseous chlorine." By Joseph William Mellor.

The rate at which active chlorine returns to the ordinary condition follows the exponential law $x = x_0 e^{-at}$, where x denotes activity at time

t , and α and x_0 are constants (α being 2.2 approximately). This is true when the activity is induced either by the electric discharge or by exposure to light.

173. "Note on the influence of certain salts and organic substances on the oxidation of guaiacum." By Miss Edith Gertrude Willcock.

The author has investigated the influence of various salts on the oxidation of guaiacum with hydrogen peroxide by determining the time necessary to produce a standard blue tint when the conditions were so adjusted that the concentration of guaiacum, peroxide, and salt, and the temperature were the same throughout the series.

It was found that the oxidation was accelerated by the chlorides of ammonium, lithium, potassium, barium, iron, and aluminium, the bromides of sodium and potassium, potassium iodide, sodium fluoride, and potassium nitrite; whereas the nitrates of ammonium, potassium, and barium, and the sulphates of sodium, potassium, and magnesium had no appreciable influence.

These results show (1) that the influence of the salt is determined by the nature of the anion, and (2) that the halogen salts as a group accelerate the oxidation.

Of the salts examined, those of the halogens alone showed a true accelerating action, for although potassium nitrite certainly accelerates the oxidation of guaiacum by hydrogen peroxide, yet as it will itself oxidise this resin in the absence of the peroxide its influence is not comparable with that of the salts which have no independent oxidising action; this remark also applies to ferric chloride.

A comparison of the salts of the halogens among themselves showed that the iodides have the greatest accelerating action, the effect of the others diminishing in the following order; namely, bromides, chlorides, and fluorides. The position of the iodides in the list may be connected with the oxidising action of hydrogen peroxide on these salts.

Salts such as aluminium chloride and sodium fluoride, which form acid solutions, have a relatively feeble accelerating power.

Ordinary "pure" aluminium chloride readily oxidises guaiacum even in the absence of peroxide, but a specially purified sample of the salt had no independent oxidising action whatever, and it increased the rate of oxidation by hydrogen peroxide only very slightly. The activity of commercial aluminium chloride is probably due to the presence of ferric chloride.

The acids of the acetic series have no accelerating action, but the metallic salts of the lower members of the series have a slight

influence, due probably to the fact that they are hydrolysed by water into free acid and base. Carbohydrates and proteids have no action.

Formaldehyde is commonly described as oxidising guaiacum, but this effect is probably due to impurities. The commercial product is an active oxidiser, turning guaiacum blue even in the absence of hydrogen peroxide, but pure formaldehyde, freshly prepared by the distillation of paraformaldehyde, has no action whatever.

Commercial glycerol readily oxidises guaiacum, turning the resin blue immediately, but in this case also the action seems to be due to impurities, for when freshly distilled under diminished pressure in the dark it has no effect by itself, although, like methyl and ethyl alcohols and ethylene glycol, it assists the accelerating action of the metallic haloids at the ordinary temperature ($15-25^{\circ}$). These substances, however, at $50-70^{\circ}$ all exert a retarding influence, and this may be due to some absorption of the available oxygen by the alcohol.

The carbohydrates dextrose, laevulose, sucrose, maltose, dextrin, starch, glycogen, and mastic decrease the accelerating action of the salts, and the proteid globulin has the same action.

The action of carbohydrates and proteids (globulins) in diminishing the accelerating power of salts is probably due to the fact that the organic substance, being itself oxidisable, absorbs a part of the oxygen which is liberated, and also to its influence on the degree of dissociation of the salt (compare Walker and Hambly, *Trans.*, 1897, 71, 61).

The effect of sucrose on the electrical conductivity of sodium chloride has been measured by Mr. Hardy, who found that the presence of 16 per cent. of this sugar in a normal solution of the salt diminished the electrical conductivity by 23 per cent. (compare *J. Physiol.*, 1903, 29, 26).

The accelerating action of the alcohols is adequately explained by their influence on the solubility of the guaiacum. When an alcoholic solution of the resin is added to water, precipitation occurs, but on the addition of more of the alcohol the precipitate redissolves. This was found to be the case with all the alcohols examined except mannitol, and this substance alone failed to accelerate the oxidation of the guaiacum.

174. "Note on the influence of potassium persulphate on the estimation of hydrogen peroxide." By John Albert Newton Friend.

It was shown in a recent communication (*Trans.*, 1904, 85, 597) that in ordinary circumstances a correct estimate of hydrogen per-

oxide is not obtained by titration with potassium permanganate. The author now shows that for every molecule of peroxide not accounted for a molecule of persulphate disappears. This observation suggests that the reaction $\text{H}_2\text{O}_2 + \text{K}_2\text{S}_2\text{O}_8 = \text{K}_2\text{SO}_4 + \text{H}_2\text{SO}_4 + \text{O}_2$ probably takes place, this change being catalytically accelerated by some oxide of manganese formed during titration.

175. "The influence of sunlight on the dissolution of gold in aqueous potassium cyanide." By William Arthur Caldecott.

The fact that the formation of potassium thiocyanate in aqueous solution, under the conditions indicated by the equation $\text{PbS} + \text{KCyanide} + \text{O} = \text{PbO} + \text{KCNS}$, is accelerated by bright sunlight was noted some years ago by Bettel and Feldtmann (*Proc. Chem. Metallurg. Soc. S. Africa*, 1896, 1, 267). In a paper published last year (*J. Chem. Metallurg. Soc. S. Africa*, 1903, 4, 51) by E. H. Johnson and the author, the analogy between potassium aurocyanide and potassium thiocyanate with regard to their formation and reduction was discussed.

The following experiments were carried out with the view of ascertaining whether sunlight accelerated the formation of potassium aurocyanide, as well as that of potassium thiocyanate.

A strip of gold foil weighing 832.5 milligrams and having a total superficial area of 852 sq. mm. was immersed in a 0.5 per cent. potassium cyanide solution, contained in a clear glass litre bottle at about 19°. In another similar glass vessel, coated with three layers of black varnish, was placed a corresponding amount of the potassium cyanide solution and a strip of gold foil weighing 900 milligrams, but with a superficial area equal to that of the other strip. The two bottles were then exposed to direct sunlight for about 5½ hours daily during five days, the loss of weight of the gold foil strips was noted, the maximum temperatures of the solutions being recorded daily. The results were as follows :

	The clear bottle.		The blackened bottle.	
	Gold dissolved in milligrams.	Temp.	Gold dissolved in milligrams.	Temp.
1st day	25.5	36°	20.0	40°
2nd day	21.0	34	17.0	38
3rd day	28.0	34	20.0	38
4th day	27.0	37	17.0	40
5th day	32.0	39	19.0	43
Daily average	26.7	36	18.6	39.8

This table shows that the rate of dissolution of the gold in the clear glass bottle was 43 per cent. greater than that in the blackened vessel, although the temperature of the solution was on an average 3.8° lower than in the former case.

The lately published researches of Berthelot (*Compt. rend.*, 1904, 139, 169) indicate that the absorption of oxygen by aqueous potassium cyanide is accelerated by sunlight. The greater rapidity with which gold dissolves in potassium cyanide solution in bright sunlight may hence be considered as being due to the liberation of more nascent cyanogen, in proportion to the additional oxygen absorbed, with the consequent increased formation of aurous cyanide.

176. "The fractional hydrolysis of amygdalinic acid. *iso*Amygdalin." By Henry Drysdale Dakin.

As amygdalinic acid, prepared by the action of hot baryta solution on amygdalin, gives racemic mandelic acid on complete hydrolysis with acids, it is therefore probably a partially racemic substance, and may be considered as being the maltoside of inactive mandelic acid. On fractional hydrolysis, it was found that the mandelic acid set free in the earlier stages of the reaction was strongly dextrorotatory, whilst that liberated at a later stage was lævorotatory. By repeated crystallisation of the magnesium salts and of the free acids derived from the products of hydrolysis, it was found possible to isolate both optically active varieties of mandelic acid in a pure state.

Starting from amygdalin, which on hydrolysis gives *l*-mandelic acid almost exclusively, it is thus possible to prepare both *d*- and *l*-mandelic acids without employing any additional optically active substance.

The production of an isomeric partially racemic amygdalin, as the result of the limited action of baryta solution on amygdalin, was suggested by J. W. Walker (*Trans.*, 1903, 83, 472), but efforts to isolate the substance were unsuccessful.

The substance has now been obtained in crystalline form, and its main properties have been investigated; it is very much more soluble in water and alcohol, has a much lower melting point and a higher specific rotation than ordinary amygdalin. The close relationship between the two substances is shown by the fact that both are similarly attacked by the enzymes, emulsin and maltase.

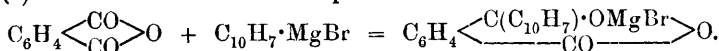
The new substance gives amygdalinic acid and ammonia on treatment with alkali, whilst with concentrated acids it yields mandelic acid, glucose, and ammonia. The mandelic acid set free on complete hydrolysis with hydrochloric acid is distinctly dextrorotatory, whereas that derived from ordinary amygdalin is lævorotatory. The suggested cause of this surprising result is that the two forms of which *iso*-

amygdalin, as a partially racemic substance, may be assumed to be composed are hydrolysed at unequal rates, and that the form which is least readily hydrolysed undergoes progressive racemisation.

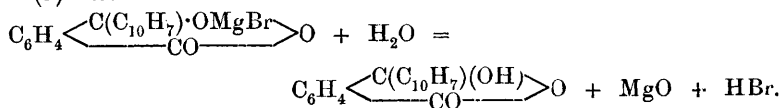
177. "The effect of anhydrides on organo-magnesium bromides. Part I. The action of phthalic anhydride on magnesium α -naphthyl bromide." By Samuel Shrowder Pickles and Charles Weizmann.

Although Grignard's reaction has been extensively used for the production of hydrocarbons, alcohols, and acids from ketones and esters, the effect of this reaction on anhydrides does not seem to have been studied. With the object of discovering another method for the preparation of certain quinones and their derivatives, the magnesium reaction was tried with magnesium α -naphthyl bromide and phthalic anhydride. The course of the reaction may be expressed as follows :

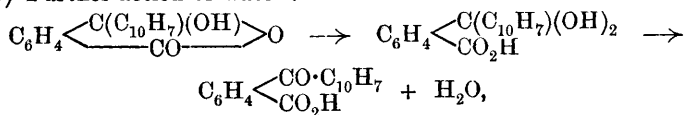
(1) Formation of additive compound :



(2) Action of water and dilute acid :



(3) Further action of water :



the product of the reaction being a keto-acid, in this case, α -naphthoyl-*o*-benzoic acid.

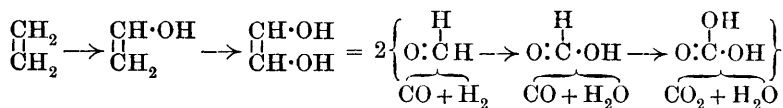
Such acids, on treatment with strong sulphuric acid, pass almost at once into quinones, the foregoing acid, for example, yielding naphth-anthraquinone.

Subsequent experiments have shown that the above reaction is capable of general application. Thus, using phthalic anhydride and bromobenzene, the authors have obtained benzoyl-*o*-benzoic acid and anthraquinone, and with phthalic anhydride and β -bromonaphthalene they have obtained β -naphthoyl-*o*-benzoic acid and naphthacene-quinone.

Experiments are now being carried out in the aliphatic series with succinic anhydride and various fatty bromides.

178. "The combustion of ethylene." By William Arthur Bone and Richard Vernon Wheeler.

The combustion of ethylene appears to be essentially a process of hydroxylation, that is, oxygen initially enters the hydrocarbon and is distributed between the carbon and hydrogen, giving rise to hydroxylated molecules, which sooner or later, according to the rapidity of the process, undergo thermal decompositions into simpler products. The stages in the combustion are represented by the following scheme :



The more salient features of the experiments may be summarised as follows :

(1) There is no preferential combustion of either carbon or hydrogen when ethylene interacts with a quantity of oxygen insufficient to burn it completely to steam and oxides of carbon. The separation of carbon or hydrogen, when it does occur, is to be entirely ascribed to secondary thermal decompositions.

(2) Formaldehyde is the most prominent intermediate oxidation product, and at low temperatures its formation is probably preceded by that of a less oxygenated product.

(3) The formation of aldehydes precedes that of steam and oxides of carbon.

(4) The stage in the combustion process at which secondary decompositions set in is determined entirely by the temperature conditions. Below the ignition point, such changes do not come into play to any appreciable extent until the stage corresponding with the formation of formic acid is reached. The greater part of this substance then decomposes into carbon monoxide and steam, whilst the remainder is further oxidised to carbonic acid, which in turn breaks down into carbon dioxide and steam. Above the ignition point, the formaldehyde produced rapidly decomposes into carbon monoxide and hydrogen.

(5) There is no separation of carbon or liberation of acetylene, even in the explosive combustion of ethylene, except when the oxygen present is insufficient to burn the hydrocarbon to formaldehyde. In such circumstances, the excess of ethylene is thermally decomposed, yielding carbon, hydrogen, methane, and traces of acetylene. Some evidence was obtained under suitable conditions of the transformation of the initial product, $\text{CH}_2 \cdot \text{CH} \cdot \text{OH}$, into the isomeric acetaldehyde, which is then independently oxidised to carbon monoxide, water, and formaldehyde, as proved in a previous paper.

The authors have not yet decided whether at low temperatures the oxygen is conveyed to the hydrocarbon directly or indirectly, but at high temperatures, as, for example, in the explosion wave, it is believed that there is a direct passage from $\begin{array}{c} \text{H} \cdot \text{C} \cdot \text{H} \\ || \\ \text{H} \cdot \text{C} \cdot \text{H} \end{array}$ to $\begin{array}{c} \text{H} \cdot \text{C} \cdot \text{OH} \\ || \\ \text{H} \cdot \text{C} \cdot \text{OH} \end{array}$, as the result of collisions between single molecules of ethylene and oxygen.

179. "The decomposition of methylcarbamide." By Charles Edward Fawsitt.

This investigation has been conducted on similar lines to that on carbamide (*Zeit. physikal. Chem.*, 1902, 41, 601), and it is found that the mechanism of the decomposition is precisely similar in the two cases, so that the theory put forward to explain the decomposition of carbamide is also applicable in the present instance.

The decomposition of methylcarbamide by acids is due to a transformation of the methylcarbamide into methylamine cyanate, which is subsequently decomposed by the acid. The initial transformation is a reaction of the first order, and the velocity coefficient at 99° is almost exactly one-half that of carbamide. In these experiments it is only the free methylcarbamide which represents the active concentration of substance decomposing at any instant. A direct hydrolysis is brought about only very slightly even by very concentrated alkali, and the reaction with pure water is very much slower than is the case with carbamide.

180. "Position isomerism and optical activity; the methyl and ethyl esters of di-*o*-, -*m*-, and -*p*-nitrobenzoyltartaric acids." By Percy Faraday Frankland and John Harger.

The authors describe the preparation and properties of the six esters in question, which were obtained by the action of the three isomeric nitrobenzoyl chlorides on methyl and ethyl tartrates respectively. The rotation of each was determined in the fused state, and over a wide range of temperature, in some cases from 15° to 180°. All these compounds, like the corresponding dibenzoyl- and ditoluyt-tartrates, are strongly lævorotatory. The *p*- and *m*-nitrobenzoyl groups were found to exercise a very great rotatory effect, the molecular rotations of the diethyl di-*p*- and di-*m*-nitrobenzoyltartrates and of the dimethyl di-*p*-nitrobenzoyltartrate being considerably in excess of those exhibited by the corresponding dibenzoyl- and ditoluyt-tartrates. The dimethyl di-*m*-nitrobenzoyltartrate, on the other hand, exhibited a molecular

rotation which, although considerably greater than that of dimethyl dibenzoyltartrate, was almost identical with that of dimethyl di-*m*-toluyltartrate.

The *o*-nitrobenzoyl group behaved in an altogether exceptional manner, its relative rotatory influence being entirely dependent on the temperature. Thus it has been previously shown by one of the authors (P. Frankland and Wharton, *Trans.*, 1896, 69, 1591) that the rotatory effect of the *o*-toluyl group is inferior to that of the benzoyl group, and it would have been anticipated, therefore, that the *o*-nitrobenzoyl radicle should exert a still smaller effect; this was actually found to be the case above 130°, but with fall of temperature its rotatory effect so rapidly increases that at 15° the latter proved to be even greater than that of the *p*-nitrobenzoyl group. This abnormal behaviour of the *o*-nitrobenzoyl group, which was only fully studied in the case of the ethyl compound, was thus limited to the superfused state, the melting point of diethyl di-*o*-nitrobenzoyltartrate being 143°. This melting point, again, is exceptional in being considerably higher than that of the meta- (95·8°) and that of the para- (124·5°) compounds respectively.

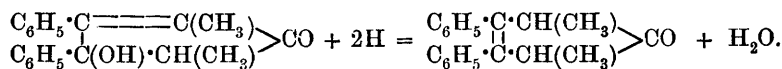
The rotation of all these compounds is very sensitive to temperature, diminishing in every case as the latter rises, much the largest temperature-coefficient being possessed by the ortho-compound.

181. "The action of nitrogen sulphide on organic substances. Part II." By Francis Ernest Francis and Oliver Charles Minty Davis.

The action of nitrogen sulphide on anisaldehyde gives rise to tri-*p*-methoxycyanidine and anisamidine sulphate, which are isolated by taking advantage of their solubilities in benzene and water respectively. An insoluble derivative of anisamidine, containing sulphur, is also produced which is very stable towards alkalis but yields anisoylanisamidine on treatment with strong acids.

182. "Reduction products $\alpha\beta$ -di thylanhydracetonebenzil, and condensation products of benzaldehydes with ketones." By Francis Robert Japp and William Maitland.

When $\alpha\beta$ -dimethylanhydracetonebenzil is boiled for a few minutes with fuming hydriodic acid, it is reduced to a *cyclopentenone* derivative (m. p. 122°):

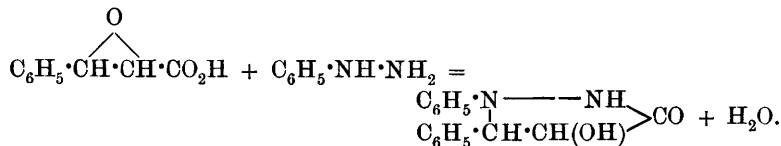


This compound is identical with that which Vorländer and Wilcke (*Ber.*, 1898, 31, 1887) obtained by the action of hydrogen chloride on dimethyldiphenyltetrahydro- γ -pyrone, but which they erroneously regard as dibenzylidenediethylketone. By further reduction with hydriodic acid, it yields the corresponding *cyclopentanone* derivative.

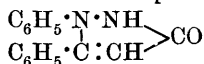
The authors have prepared various alkyl derivatives of tetrahydro- γ -pyrone by the usual method of condensing benzaldehyde with aliphatic ketones, and have studied their reactions, especially with the view of obtaining *cyclopentenone* derivatives.

183. "Interaction of sodium phenylglycidate with phenylhydrazine." By Francis Robert Japp and William Maitland.

When sodium phenylglycidate is heated with phenylhydrazine in alcoholic solution at 100° , 4-hydroxy-1:5-diphenyl-3-pyrazolidone (m. p. 173.5°) is obtained in the form of its sodium salt:



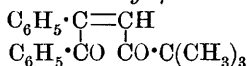
By the action of heat or of dehydrating agents, hydroxydiphenylpyrazolidone is converted into 1:5-diphenyl-3-pyrazolone,



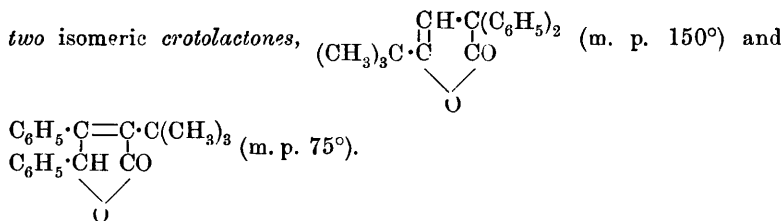
(m. p. 252°), previously obtained by Knorr (*Ber.*, 1887, 20, 1107) by distilling cinnamoylphenylhydrazine.

184. " α -Benzoyl- β -trimethacetylstyrene." By Francis Robert Japp and William Maitland.

The authors have obtained α -benzoyl- β -trimethacetylstyrene,



(m. p. 115°), by the action of potassium hydroxide on a mixture of benzil and methyl *tert*-butyl ketone. In its reactions, it closely resembles $\alpha\beta$ -dibenzoylstyrene (Japp and Klingemann, *Trans.*, 1890, 57, 662), except that, on heating, it is converted into a mixture of



185. "Olefinic ketonic compounds." By Siegfried Ruhemann.

Rabe (*Ber.*, 1902, **35**, 3947) stated that the additive compound of aniline and ethyl benzylideneacetoacetate melted at 78° instead of at 105° (erroneously printed as 103°) as found by Ruhemann and Watson (*Trans.*, 1904, **85**, 1170). On re-examination, it was found that the melting point could be raised to $106-107^\circ$, which closely agreed with that given by Francis (*Ber.*, 1903, **36**, 937) for the substance he obtained by combining benzylideneaniline with ethyl acetoacetate.

The author also examined the action of potassium cyanide on benzylideneacetylacetone and ethyl benzylideneacetoacetate respectively, and found that in the first case cyanobenzylacetylacetone, $\text{C}_6\text{H}_5 \cdot \text{CH}(\text{CN}) \cdot \text{CH}(\text{CO} \cdot \text{CH}_3)_2$ (m. p. $127-128^\circ$), and, in the other, ethyl cyanobenzylacetoacetate, $\text{C}_6\text{H}_5 \cdot \text{CH}(\text{CN}) \cdot \text{CH}(\text{CO} \cdot \text{CH}_3) \cdot \text{CO}_2 \cdot \text{C}_2\text{H}_5$, are produced. On hydrolysis with caustic potash, the former nitrile furnishes phenylacetopropionic acid, $\text{C}_6\text{H}_5 \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_3$, whilst ethyl cyanobenzylacetoacetate yields a mixture of phenylacetopropionic and phenylsuccinic acids. Under the influence of concentrated sulphuric acid, cyanobenzylacetylacetone is transformed into phenyldiacetopropionic acid, $\text{C}_6\text{H}_5 \cdot \text{CH}(\text{CO}_2\text{H})\text{CH}(\text{CO} \cdot \text{CH}_3)_2$ (m. p. $149-150^\circ$); ethyl cyanobenzylacetoacetate, on the other hand, furnishes the dihydropyrone derivative, $\text{NH}-\text{C}(\text{CH}_3) \begin{array}{c} \text{CO} \cdot \text{CH}(\text{C}_6\text{H}_5) \end{array} \rangle \text{C} \cdot \text{CO}_2 \cdot \text{C}_2\text{H}_5$.

The mode of formation and the properties of cinnamylideneacetylacetone, $\text{C}_6\text{H}_5 \cdot \text{CH} : \text{CH} : \text{CH} : \text{C}(\text{CO} \cdot \text{CH}_3)_2$ (m. p. $103-104^\circ$), are also described. This di-olefinic ketone, on exposure to light, undergoes a change similar to that occurring in the case of cinnamylidenemalonic acid (Liebermann, *Ber.*, 1895, **28**, 1440; Riiber, *Ber.*, 1902, **35**, 2411), and yields a colourless substance (m. p. $158-159^\circ$) which has double the molecular weight of cinnamylideneacetylacetone. These two compounds are still under examination.

186. " Δ^{α} -Oleic acid." By Henry Rondel Le Sueur.

In a former communication (*Trans.*, 1904, 85, 827), the author stated that he was engaged in the preparation of an isomeride of oleic acid containing the double linking between the α - and β -carbon atoms, and, although the work is not complete, the appearance of a paper by G. Ponzio (*Gazzetta*, 1904, 34, ii, 77; *Chem. Centr.*, 1904, ii, 691) on the same subject necessitates the publication of the results so far obtained.

Δ^{α} -Oleic acid, $C_{15}H_{31}\cdot CH:CH\cdot CO_2H$, obtained by the action of alcoholic potash on α bromostearic acid, crystallises from light petroleum in long, flat needles melting at $58-59^{\circ}$; its *ethyl ester* melts at $25-26^{\circ}$. The acid, on oxidation with potassium permanganate, yields $\alpha\beta$ -dihydroxystearic acid melting at 126° , which on further oxidation yields palmitic acid, thereby proving the position of the double linking.

187. "Action of magnesium alkyl halides on derivatives of camphor." By Martin Onslow Forster.

The action of magnesium alkyl halides on derivatives of camphor is not always normal, and several interesting changes have been observed.

The compound, $C_{12}H_{22}O_2$, from camphorquinone and magnesium methiodide is a volatile, colourless compound, dissolving readily in organic media and very sparingly in water, from which it crystallises in minute, transparent prisms and needles melting at 132° . A 2 per cent. solution in absolute alcohol is optically inactive.

The compound, $C_{11}H_{19}O_2N$, from isonitrosocamphor and magnesium methiodide is soluble in acids and alkalis, forming colourless solutions; it separates from boiling water as a crystalline powder and melts at 180° .

The compound, $C_{11}H_{19}O_3N$, from nitrocamphor and magnesium methiodide is insoluble in sodium carbonate solution, but dissolves in aqueous sodium hydroxide; it crystallises from petroleum in lustrous leaflets melting at 83° .

The compound from hydroxymethylenecamphor and magnesium methiodide is a colourless, fragrant oil which boils at $234^{\circ}/765$ mm., has sp. gr. 0.9639, and $[\alpha]_D$ 170.8° . It is insoluble in aqueous sodium hydroxide, and gives no coloration with ethereal ferric chloride.

188. "Sulphonchloroalkylamides." By Frederick Daniel Chattaway.

In the course of an investigation of nitrogen halogen derivatives of the sulphonamides, a number of compounds yielded by various methyl, ethyl, and benzyl derivatives of the sulphonamides have been obtained. All the sulphonalkylamides are readily converted by a solution of hypochlorous acid into the corresponding chloroamides, $\text{RSO}_2 \cdot \text{NHR}' + \text{HOCl} = \text{RSO}_2 \cdot \text{NClR}' + \text{H}_2\text{O}$. Those containing methyl and ethyl groups are comparatively stable, whereas those in which benzyl occurs undergo spontaneous decomposition after a few hours; even when kept in dry air, chlorine and hydrogen chloride are liberated, while a pungent odour, resembling that of benzaldehyde, becomes apparent. When rapidly heated, they all decompose with evolution of gas, but without explosion. Like the sulphonchloroamides, they are very reactive, and promise to be of considerable value in the synthesis of secondary amines containing different alkyl groups.

The following compounds are typical examples of a long series of these substances which has been prepared. Benzenesulphonchloromethylamide, $\text{C}_6\text{H}_5 \cdot \text{SO}_2 \cdot \text{NCl} \cdot \text{CH}_3$, colourless, short rhombs, m. p. 81° ; benzenesulphonchloroethylamide, $\text{C}_6\text{H}_5 \cdot \text{SO}_2 \cdot \text{NCl} \cdot \text{C}_2\text{H}_5$, colourless plates, m. p. 52° ; benzenesulphonchlorobenzylamide, $\text{C}_6\text{H}_5 \cdot \text{SO}_2 \cdot \text{NCl} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_5$, colourless, slender prisms, m. p. 109° ; *p*-toluenesulphonchloromethylamide, $\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{NCl} \cdot \text{CH}_3$, colourless prisms, m. p. 82° ; *m*-nitrobenzenesulphonchloromethylamide, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{NCl} \cdot \text{CH}_3$, pale yellow, four-sided plates, m. p. 136° ; α -naphthalenesulphonchloromethylamide, $\text{C}_{10}\text{H}_7 \cdot \text{SO}_2 \cdot \text{NCl} \cdot \text{CH}_3$, colourless, six-sided prisms, m. p. 78° ; α -naphthalenesulphonchlorobenzylamide, $\text{C}_{10}\text{H}_7 \cdot \text{SO}_2 \cdot \text{NCl} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_5$, very pale yellow prisms, m. p. 94° ; β -naphthalenesulphonchloromethylamide, colourless prisms, m. p. 91° ; β -naphthalenesulphonchloropropylamide, $\text{C}_{10}\text{H}_7 \cdot \text{SO}_2 \cdot \text{NCl} \cdot \text{C}_3\text{H}_7$, colourless plates, m. p. 86° .

RESEARCH FUND.

A Meeting of the Research Fund Committee will be held in December next. Applications for grants, to be made on forms which can be obtained from the Assistant Secretary, must be received on or before Monday, December 5th, 1904.

At the next ordinary meeting, on **Wednesday, November 16th, 1904**, at **5.30 p.m.**, the following papers will be communicated :

"The isomerism of the amidines of the naphthalene series." By R. Meldola and J. H. Lane.

"Theory of the production of mercurous nitrite and of its conversion into various mercury nitrates." By P. C. Rây.

"Amidechloroiodides." By G. D. Lander.

"A new synthesis of *isocapro*lactone and some derivatives." By D. T. Jones and G. Tattersall.

"The influence of substitution in the nucleus on the rate of oxidation of the side-chain. Part II. Oxidation of the halogen derivatives of toluene." By J. B. Cohen and J. Miller.

"The halogen derivatives of naphthacenequinone." By S. S. Pickles and C. Weizmann.

"Constitution of pyrazolidone derivatives." By B. Prentice.

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