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V.—*Interaction of* 1 : 2-*Diketones with Primary Amines of the General Formula*, $R'\cdot CH_2\cdot NH_2$.

By FRANCIS R. JAPP, F.R.S., and W. B. DAVIDSON, M.A., B.Sc.

INTRODUCTION.

THE action of paraffinoid amines on 1 : 2-diketones appears to have been very little studied. Zincke and Hof (*Ber.*, **12**, 1644), by heating phenanthraquinone with methylamine, obtained a base to which they assigned the formula $C_{14}H_8(N\cdot CH_3)_2$, together with another compound, the composition of which they could not determine with certainty. Henius (*Ammoniakderivate des Benzils*, Marburg, 1881), desirous of studying the analogous interaction with benzil, heated that substance with methylamine, but obtained only a resinous product.

We shall show in the present paper that Zincke and Hof's base has not the foregoing composition. We have not repeated Henius's experiment with benzil and methylamine; but we find that benzil and ethylamine, under suitable conditions, readily yield a crystallised product.

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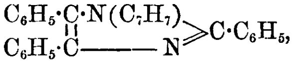
We first, however, investigated the interaction of benzil and benzylamine. When these two substances were heated together at 100°, a product was obtained from which we could isolate tetraphenylazine, $C_{28}H_{20}N_2$ (m. p. 246°), and a feebly basic compound melting at 164° and having the formula $C_{28}H_{22}N_2$; the latter substance being formed according to the equation,

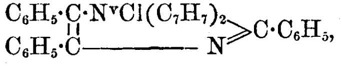
$$C_{14}H_{10}O_2 + 2C_6H_5\cdot CH_2\cdot NH_2 = C_{28}H_{22}N_2 + 2H_2O + H_2.$$

When zinc chloride was added to the mixture of benzil and benzylamine before heating, the same two compounds were obtained, but, in addition, a chloride of the formula $C_{35}H_{29}N_2Cl$ (m. p. 253°), formed according to the equation,

$$2C_{14}H_{10}O_2 + 6C_6H_5\cdot CH_2\cdot NH_2 + ZnCl_2 = 2C_{35}H_{29}N_2Cl + 2NH_3 + Zn(OH)_2 + 2H_2O + 2H_2.$$

As the difference between the formula of the chloride, $C_{35}H_{29}N_2Cl$, and that of the base, $C_{28}H_{22}N_2$, is C_7H_7Cl, which might represent a molecule of benzylic chloride, we heated the base with benzylic chloride, and found that these two substances readily united to form the chloride $C_{35}H_{29}N_2Cl$. The base was therefore a tertiary amine, and the chloride was a quaternary chloride.

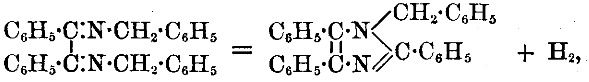
Suspecting that these two compounds were benzyl-derivatives of lophine, we next heated lophine with benzylic chloride. Both compounds were formed in this interaction. The base $C_{28}H_{22}N_2$ is therefore *benzyllophine*,  $\begin{array}{l} C_6H_5\cdot C\cdot N(C_7H_7) \\ \quad \| \\ C_6H_5\cdot C\text{———}N \end{array} \!\!> C\cdot C_6H_5$, and the chloride, $C_{35}H_{29}N_2Cl$, is *dibenzyllophonium chloride*,



$$\begin{array}{l} C_6H_5\cdot C\cdot N^vCl(C_7H_7)_2 \\ \quad \| \\ C_6H_5\cdot C\text{————}N \end{array} \!\!> C\cdot C_6H_5,$$

the latter corresponding with Kühn's diethyllophonium iodide.[*]

When a mixture of benzil and benzylamine is dissolved in ether, and allowed to stand at the ordinary temperature, drops of water speedily separate, and, on allowing the ether to evaporate spontaneously, a gummy, uncrystallisable mass remains, which is probably the first stage in the condensation of benzil with benzylamine since, on heating at 100°, it yields benzyllophine. The change,



$$\begin{array}{l} C_6H_5\cdot C{:}N\cdot CH_2\cdot C_6H_5 \\ \quad | \\ C_6H_5\cdot C{:}N\cdot CH_2\cdot C_6H_5 \end{array} = \begin{array}{l} C_6H_5\cdot C\cdot N\diagup CH_2\cdot C_6H_5 \\ \quad \| \qquad\quad > C\cdot C_6H_5 \\ C_6H_5\cdot C\cdot N\diagup \end{array} + H_2,$$

is not without analogy. Thus, as Wallach has shown, the imidochloride obtained by the action of phosphorus pentachloride on

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[*] Called by Kühn "diethyllophinium iodide;" but we adopt Victor Meyer's suggestion (*Ber.*, **27**, 505) that the names of all quaternary ammonium compounds and their analogues should end in "onium."

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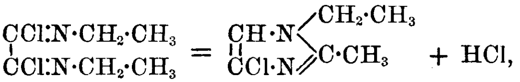
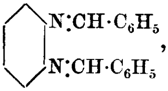
diethyloxamide parts with hydrochloric acid yielding a base, chloroxalethyline, which, as was pointed out by one of us (*Ber.*, **15**, 2420), has the constitution of a chlorinated glyoxaline (imidazole) derivative,



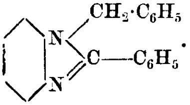
$$\begin{matrix} CCl{:}N\cdot CH_2\cdot CH_3 \\ | \\ CCl{:}N\cdot CH_2\cdot CH_3 \end{matrix} = \begin{matrix} CH\cdot N\diagup^{CH_2\cdot CH_3} \\ \| \quad \diagdown C\cdot CH_3 \\ CCl\cdot N\diagup\!\!\diagup \end{matrix} + HCl,$$

the position of the chlorine atom in the imidazole being uncertain.*

Again, in the case of the condensation products of orthodiamines with aldehydes, discovered by Ladenburg, the constitution of which was first explained by Hinsberg (*Ber.*, **19**, 2025), an analogous transformation occurs. Thus orthodiamidobenzene and benzaldehyde yield, instead of



, the tertiary imidazole



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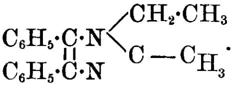
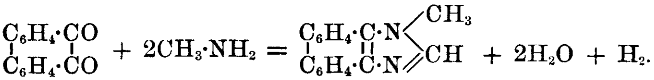
In order to ascertain whether the action of purely paraffinoid amines with benzil resembled that of benzylamine, we heated benzil with ethylamine and obtained N-ethyldiphenyl-μ-methyl-imidazole,



$$\begin{matrix} C_6H_5\cdot C\cdot N\diagup^{CH_2\cdot CH_3} \\ \| \quad \diagdown C - CH_3 \\ C_6H_5\cdot C\cdot N \end{matrix}.$$

The quaternary chloride was also formed, but we did not succeed in isolating it in a state of purity. The constitution of the tertiary imidazole was proved by synthesising the compound from Japp and Wynne's diphenyl-μ-methyl-imidazole and ethylic iodide. It was also proved to be a tertiary amine by combining it directly with ethylic iodide.

As the results obtained by Zincke and Hof (*loc. cit.*) in studying the action of methylamine on phenanthraquinone differed from those which we had arrived at with benzil, we repeated their work. We had no difficulty in preparing the base described by them, but found that it gave, on analysis, figures pointing to the formula $C_{16}H_{12}N_2$, instead of $C_{16}H_{14}N_2$, as adopted by them. (No analyses are given by Zincke and Hof in the paper referred to.) The interaction with phenanthraquinone is, therefore, analogous to that with benzil, and the compound is, in all probability, N-*methyl-diphenylene-imidazole*,



$$\begin{matrix} C_6H_4\cdot CO \\ | \qquad | \\ C_6H_4\cdot CO \end{matrix} + 2CH_3\cdot NH_2 = \begin{matrix} C_6H_4\cdot C\cdot N\diagup^{CH_3} \\ | \qquad \| \quad \diagdown CH \\ C_6H_4\cdot C\cdot N\diagup\!\!\diagup \end{matrix} + 2H_2O + H_2.$$

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* In the original of the passage quoted, chloroxalmethyline is employed as an illustration, but the argument is of course identical.

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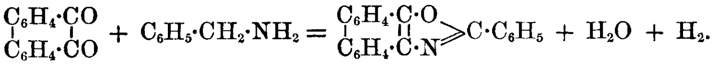
An attempt to synthesise diphenylene-imidazole by the interaction of phenanthraquinone, formaldehyde, and ammonia, in order to prepare from it the foregoing compound, led to no result.

Phenanthraquinone and benzylamine give a different interaction, forming diphenylene-μ-phenyl-oxazole according to the equation



$$\begin{array}{l} C_6H_4\cdot CO \\ | \qquad\quad | \\ C_6H_4\cdot CO \end{array} + C_6H_5\cdot CH_2\cdot NH_2 = \begin{array}{l} C_6H_4\cdot C\cdot O \\ | \qquad\quad \| \\ C_6H_4\cdot C\cdot N \end{array}\!\!>C\cdot C_6H_5 + H_2O + H_2.$$

At the same time, a sparingly soluble compound crystallising in bronze-coloured, microscopic, rectangular prisms is obtained, the exact composition of which we were unable to ascertain.

Diphenylene-μ-phenyl-oxazole was originally prepared by Japp and Wilcock (Trans., 1880, **37**, 668) by the interaction of phenanthraquinone, benzaldehyde, and ammonia, and named by them *benzenylamidophenanthrole*.

EXPERIMENTAL PART.

1. *Benzil and Benzylamine.*

The interaction of these two compounds was studied both with and without the addition of zinc chloride. We shall describe only the former method, as it gave the better result and furnished, moreover, a compound which was not otherwise obtained.

40 grams of benzil, mixed with 16 grams of powdered zinc chloride, were introduced into a flask, and 40 grams of benzylamine were added. The mixture became dark red, and considerable heat was evolved, due to the combination of the benzylamine with the zinc chloride. The flask was then heated at 100° for 40 hours, immersing it up to the neck in the water bath, as otherwise an equable heating of the pasty contents could not be effected. There was considerable frothing, ammonia being evolved during the process, and the colour of the mixture gradually changed from red to yellow. The product was then digested with boiling alcohol which dissolved everything except a white pulverulent substance; this proved to be a mixture of zinc hydroxide with a little tetraphenylazine. Acetic acid was then added in quantity sufficient nearly to clear the liquid; the still undissolved particles could then be seen to consist of slender needles; they were separated by filtration and identified as tetraphenylazine (ditolaneazotide), $C_{28}H_{20}N_2$, by their crystalline form, their melting point (247·5°), and the bright red coloration which they gave with concentrated sulphuric acid. The quantity obtained was 1·5 grams.

The formation of this compound may be readily accounted for. The other actions, occurring simultaneously (see Introduction), involve the elimination of hydrogen and ammonia; the former re-

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duces a portion of the benzil to benzoïn, the latter converts the benzoïn into tetraphenylazine (compare Japp and Wilson, Trans., 1886, **49**, 829).

The alcoholic filtrate from the tetraphenylazine was concentrated by boiling, and then mixed with about four times its volume of ether. On standing, the liquid deposited lustrous crystals, of octahedral habit, whilst a substance, crystallising in square plates (see later), remained in the mother liquor. (If, as occasionally happened, some of these plates separated along with the octahedra, they could readily be removed by boiling the mixture of crystals with benzene, in which they dissolve readily, whilst the octahedra are quite insoluble.) The octahedra effloresced rapidly when exposed to air, and smelt strongly of ether; they contained ether of crystallisation. Freed from the ether, they melted at 248°. They contained both zinc and chlorine. The analyses, given later, showed that the compound was a double chloride of zinc and an organic base. The yield in the experiment here described was 17 grams.

A quantity of the octahedral crystals was dissolved in boiling alcohol, and the zinc was precipitated by the addition of aqueous sodium carbonate. The excess of sodium carbonate and the sodium chloride formed were thus mostly precipitated along with the zinc. The filtered and concentrated liquid deposited colourless, prismatic crystals, melting, when rapidly heated, at 253°. They were insoluble in water and in benzene, readily soluble in boiling alcohol. When treated with concentrated sulphuric acid, they evolved hydrochloric acid. A solution in alcohol gave, with silver nitrate, a precipitate of silver chloride. The chlorine is not removed by ammonia, although, as we shall show later, heating the compound with alcoholic caustic potash displaces the chlorine by hydroxyl. The substance, which is the chloride of a quaternary base, was purified by recrystallisation from alcohol and dried over sulphuric acid, as it decomposes slowly at a temperature slightly above 100°. It does not contain solvent of crystallisation. Analysis gave figures agreeing with the formula $C_{35}H_{29}N_2Cl$.

0·1590 gave 0·4770 CO_2 and 0·0823 H_2O. C = 81·82; H = 5·75.
0·1340 „ 0·4010 CO_2 „ 0·0700 H_2O. C = 81·61; H = 5·80.
0·2672 „ 12·4 c.c. moist nitrogen at 10° and 746·5 mm. N = 5·46.
0·8714 „ 0·2521 AgCl. Cl = 7·18.
$C_{35}H_{29}N_2Cl$ requires C = 81·95; H = 5·66; N = 5·46; Cl = 6·93 p. c.

Two other methods were employed in isolating the quaternary chloride from the zinc double compound. In one of these the latter compound was dissolved in hot alcohol and the zinc precipitated with ammonium sulphide; the filtered solution, after concentration, de-

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posited the quaternary chloride. In the other, sodium acetate was added to the hot alcoholic solution, which was then diluted with water; the quaternary chloride slowly separated in a crystalline form, the zinc remaining in solution as acetate. Precipitation with sodium carbonate was found, however, to give the best results.

An alcoholic solution of the quaternary chloride gave, on addition of platinic chloride, also dissolved in alcohol, an orange-coloured, crystalline precipitate of the platinum salt. Under the microscope, the crystals were seen to consist of prisms terminated by pyramids. Sometimes these prisms were single, sometimes two were grouped into a right-angled cross, sometimes a third prism intersected the cross at right angles to its plane, forming a figure like the axes in the cubical system. We describe these forms thus particularly, inasmuch as we afterwards employed this salt in identifying the quaternary chloride. As the salt decomposes slowly at 80°, the air-dried substance was used for analysis.

1·2620 gave 0·1795 Pt. Pt = 14·22.

$(C_{35}H_{29}N_2Cl)_2PtCl_4$ requires Pt = 14·29 per cent.

By bringing together the chloride, $C_{35}H_{29}N_2Cl$, with zinc chloride in alcoholic solution, the zinc double compound could be regenerated. From alcohol, the double compound was deposited in well-formed crystals, without solvent of crystallisation. Although decomposed, as already mentioned, by sodium acetate, it can be recrystallised from glacial acetic acid without change.

A full analysis of the zinc double compound, as obtained in the original interaction, was made before its true nature had been ascertained, and before the organic chloride had been isolated from it. The substance was dried at 100°, so as to expel the ether of crystallisation. Of the various determinations, the carbon alone is not concordant, possibly owing to a difficulty in burning the substance; but the analysis was not repeated, as the quaternary chloride itself had meanwhile been obtained and analysed.

0·2494 gave 0·6544 CO_2 and 0·1150 H_2O. C = 71·56; H = 5·12.
0·3005 „ 13·2 c.c. moist nitrogen at 10° and 728·5 mm. N = 5·04.
6·2180 „ 0·4480 ZnO. Zn = 5·78.
1·1223 „ 0·5501 AgCl. Cl = 12·22.
$(C_{35}H_{29}N_2Cl)_2ZnCl_2$ requires C = 72·36; H = 4·99; N = 4·82; Zn = 5·60; Cl = 12·23 per cent.

The determination of the ether of crystallisation in the crystallised compound was a matter of some difficulty, owing to the rapidity with which the substance effloresced, and also owing to the fact that, occasionally, clear crystals, without solvent of crystallisation, were found among those which had been used for the determination, the

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latter form being, as already stated, that in which the double compound is deposited from alcohol without the addition of ether. The best result—only approximate, however—was obtained by taking for the determination a considerable weight (over 16 grams) of the substance deposited from alcohol on the addition of ether, avoiding the presence of small crystals, which were removed by sifting through coarse wire gauze, after the whole had been quickly dried on filter paper. The salt lost, on heating at 100°, 14·59 per cent., whilst the formula $(C_{35}H_{29}N_2Cl)_2ZnCl_2,3(C_2H_5)_2O$ requires 16·05 per cent. As the crystals had been deposited from a mixture of alcohol and ether, it was necessary to prove that the solvent of crystallisation consisted of ether only. For this purpose, some of the crystals, air-dried for a short time, were introduced into a distilling flask and the solvent of crystallisation distilled off on the water bath. The boiling point of the distillate was determined by Chapman Jones's method, from the vapour tension, and found to be 35°.

The ethereal-alcoholic mother liquor, containing those products of the original interaction which remained after the removal of the zinc double salt, was freed from its ether by distillation. The resulting alcoholic solution deposited, on long standing, yellow, square plates of a new compound, mixed, however, with needles of tetraphenylazine; the latter were removed by levigation. By recrystallising the square plates from benzene, in which they were readily soluble, and afterwards from alcohol, they were obtained colourless, and melted constantly at 165°. The substance is dimorphous; from concentrated solutions, it separates in slender needles; from dilute solutions, in square plates, as above; the presence of impurity appears to favour crystallisation in the latter form. Either form can be readily converted, by recrystallisation, into the other. The yield was about 20 grams. Analysis of the square plates dried at 100° gave figures agreeing with the formula $C_{28}H_{22}N_2$.

0·1358 gave 0·4325 CO_2 and 0·0709 H_2O. C = 86·86; H = 5·80.
0·1362 „ 0·4338 CO_2 „ 0·0722 H_2O. C = 86·86; H = 5·89.
0·1912 „ 11·90 c.c. moist nitrogen at 11° and 739 mm. N = 7·21.
0·1920 „ 12·13 „ „ „ 11·5° and 732·5 mm. N = 7·24.
$C_{28}H_{22}N_2$ requires C = 87·05; H = 5·70; N = 7·25 per cent.

The compound is insoluble in aqueous acids, but it nevertheless acts as a weak monacid base, forming a platinichloride. The latter is slowly deposited in large, lustrous, orange-coloured, oblique prisms, containing 3 mols. of alcohol of crystallisation, when concentrated solutions of the base and of platinic chloride (H_2PtCl_6) in absolute alcohol are mixed and allowed to stand. The crystals effloresced when exposed to the air. For analysis, they were air-dried for a

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short time. The figures for alcohol of crystallisation were not very concordant.

1·0882 (containing alcohol) lost, at 95°, 0·1250. $C_2H_5{\cdot}OH = 11{\cdot}49$.
$(C_{28}H_{22}N_2)_2H_2PtCl_6,3C_2H_5{\cdot}OH$ requires $C_2H_5{\cdot}OH = 10{\cdot}46$ per cent.
0 9632 (freed from alcohol) gave 0·1592 Pt. Pt = 16·53.
$(C_{28}H_{22}N_2)_2H_2PtCl_6$ requires Pt = 16·50 per cent.

The composition of this salt confirms the molecular formula, $C_{28}H_{22}N_2$, for the base.

Conversion of the Base, $C_{28}H_{22}N_2$, *into the Quaternary Chloride,* $C_{35}H_{29}N_2Cl$.—4 grams of the base were boiled for an hour with 8 grams of benzylic chloride in a flask fitted with a reflux condensing tube. During the process, a solid substance separated in acicular crystals. The product was digested with ether; the insoluble portion was separated by filtration, washed with ether, and dissolved in boiling alcohol. The alcoholic solution deposited crystals identical in form with those of the quaternary chloride, $C_{35}H_{29}N_2Cl$, mixed, however, with some of the unaltered compound, $C_{28}H_{22}N_2$; the latter substance was removed by boiling the mixture of crystals with benzene. The portion insoluble in benzene was purified by recrystallisation from alcohol until it showed the constant melting point of 253°. It was indistinguishable in appearance from the quaternary chloride obtained from benzil, benzylamine, and zinc chloride. In alcoholic solution, it gave a precipitate of silver chloride on the addition of alcoholic silver nitrate. A nitrogen determination confirmed the identity of the two substances.

0·3190 gave 14·7 c.c. moist nitrogen at 10° and 755 mm. N = 5·48.
$C_{35}H_{29}N_2Cl$ requires N = 5·46 per cent.

In addition, the platinum salt was prepared. It exhibited, under the microscope, the characteristic forms already described.

Synthesis of the Compounds $C_{28}H_{22}N_2$ *and* $C_{35}H_{29}N_2Cl$ *from Lophine.*—10 grams of lophine were boiled for an hour with 20 grams of benzylic chloride. Hydrochloric acid was evolved during the process. The product, which consisted of a crystalline mass saturated with excess of benzylic chloride, was washed several times with ether, uniting the ethereal washings. The crystalline portion was then recrystallised from alcohol until it melted constantly at 253°. It had all the properties of the quaternary chloride, $C_{35}H_{29}N_2Cl$, gave a precipitate with silver nitrate, and yielded the characteristic platinum salt. Nitrogen was determined with the following result.

0·2724 gave 12·8 c.c. moist nitrogen at 8° and 739·5 mm. N = 5·51.
$C_{35}H_{29}N_2Cl$ requires N = 5·46 per cent.

The ethereal washings were then heated to expel the ether, after

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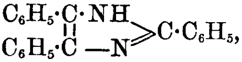
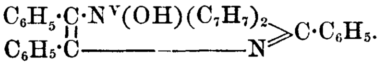
which the excess of benzylic chloride was distilled off at 100° under reduced pressure. The residue, which was brown and crystalline, was dissolved in boiling alcohol. The solution deposited the two forms of the compound $C_{28}H_{22}N_2$, square plates and needles. The melting point was found to be 164·5° instead of 165°. A nitrogen determination, made with the square plates, gave figures agreeing with the expected formula.

0·2395 gave 15·3 c.c. moist nitrogen at 6° and 739·5 mm. N = 7·57.
$C_{28}H_{22}N_2$ requires N = 7·25 per cent.

The quantity of this compound obtained was very small, as, when formed, it is mostly converted into the quaternary chloride.

The two compounds are, therefore, benzyl derivatives of lophine (triphenylimidazole),  $\begin{matrix} C_6H_5\cdot C\cdot NH \\ \Vert \\ C_6H_5\cdot C - N \end{matrix} > C\cdot C_6H_5$, the base, $C_{28}H_{22}N_2$, being *benzyllophine*, and the chloride, $C_{35}H_{29}N_2Cl$, *dibenzyllophonium chloride*, as formulated in the Introduction to this paper.

Dibenzyllophonium Hydroxide.—8 grams of dibenzyllophonium chloride were dissolved in hot alcohol, 24 grams of powdered caustic potash were added, and the whole was digested on the water bath for 40 hours.* During the process potassium chloride separated. The alcohol was then driven off, and the residue treated with water, which dissolved everything except a brown substance. This was separated, first digested with a little alcohol, which removed most of the brown colour, and then dissolved in boiling alcohol. It separated in yellow square plates, which were purified by recrystallisation from boiling alcohol until they melted constantly at 170°. The substance is but sparingly soluble in alcohol, even at the boiling point of the solvent; readily, however, in boiling benzene, separating from it, on cooling, in forms identical with those obtained from alcohol, but always contaminated with pale brown needles of another substance (see later), so that benzene cannot be employed in its purification. The yellow colour is not removed by recrystallisation, or by treatment with animal charcoal. Analysis showed that the substance had the composition of *dibenzyllophonium hydroxide*,



$$\begin{matrix} C_6H_5\cdot C\cdot N^{V}(OH)(C_7H_7)_2 \\ \Vert \\ C_6H_5\cdot C \text{———————} N \end{matrix} > C\cdot C_6H_5.$$

0·1513 gave 0·4715 CO_2 and 0·0852 H_2O. C = 84·99; H = 6·26.
0·2517 ,, 11·9 c.c. moist nitrogen at 6° and 768·5 mm. N = 5·82.
$C_{35}H_{30}N_2O$ requires C = 85·02; H = 6·07; N = 5·67 per cent.

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* This long heating was possibly unnecessary, and, owing to the susceptibility of dibenzyllophonium hydroxide to aërial oxidation (see later), may even have diminished the yield.

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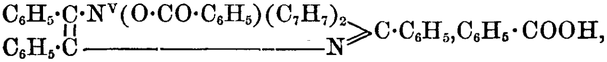
On dissolving the substance in alcoholic hydrochloric acid, the yellow colour disappeared, and the solution deposited colourless crystals which, by their form, melting point, and the characteristic platinum salt which they yielded, were identified as *dibenzyllophonium chloride.*

Benzoates of Dibenzyllophonium.—We have already mentioned that when dibenzyllophonium hydroxide is recrystallised from benzene, the solution deposits, along with the yellow, square plates of the hydroxide, pale brown needles of a different compound. Imagining that this was an impurity, we separated mechanically the crystals of the hydroxide, and redissolved them in benzene; but again the solution deposited a mixture of the two kinds; indeed, we found that, by repeatedly recrystallising the hydroxide from benzene, it could be completely transformed into the needles. The solubility of the latter was exactly the reverse of that of the hydroxide; they were sparingly soluble in benzene and readily in alcohol; for this reason, when alcohol was used in recrystallising the hydroxide, their presence was not perceived.

By recrystallising the needle-shaped compound from benzene, we obtained it almost colourless. It melted at 175·5°. Analysis gave figures agreeing with the formula $C_{49}H_{40}N_2O_4$.*

0·1708 gave 0·5111 CO_2 and 0·0880 H_2O. C = 81·61; H = 5·72.
0·1286 „ 0·3855 CO_2 and 0·0647 H_2O. C = 81·75; H = 5·59.
0·2547 „ 8·5 c.c. moist nitrogen at 7·5° and 759·5 mm. N = 4·04.
$C_{49}H_{40}N_2O_4$ requires C = 81·67; H = 5·56; N = 3·89 per cent.

This would be the composition of a *dibenzyllophonium dibenzoate* of the formula



$$\begin{array}{l} C_6H_5\cdot C\cdot N^{V}(O\cdot CO\cdot C_6H_5)(C_7H_7)_2 \\ \quad\;\| \\ C_6H_5\cdot C\text{———————————}N \end{array}\!\!>\!C\cdot C_6H_5, C_6H_5\cdot COOH,$$

formed from the hydroxide and benzoic acid according to the equation

$$C_{35}H_{29}N_2\cdot OH + 2C_6H_5\cdot COOH = C_{49}H_{40}N_2O_4 + H_2O.$$

In order to test the correctness of this supposition, a small quantity of dibenzyllophonium hydroxide was dissolved in benzene, after which twice its molecular proportion of benzoic acid was added. The yellow colour of the hydroxide disappeared instantly, and the liquid deposited colourless, needle-shaped crystals of the dibenzoate melting at 175°. They were purer than those obtained by the previous

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* In the portion of this work relating to the interaction of benzil and benzylamine, the deducing of these somewhat complex formulæ from the results of analysis was, of course, greatly facilitated by the consideration that the number of carbon atoms in the molecule of any compound formed would almost certainly be some multiple of 7.

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method. A nitrogen determination gave 4·00 per cent. ($C_{49}H_{40}N_2O_4$ requires N = 3·89 per cent.).

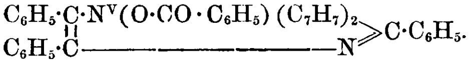
The obvious explanation of the formation of this compound during the recrystallisation of the hydroxide from benzene was that a portion of the hydroxide had been converted by aërial oxidation into benzoic acid, the latter substance then interacting with the unchanged hydroxide according to the foregoing equation. This view was readily tested. Into each of two tubes filled with and standing over mercury, 0·3 gram of the hydroxide was introduced, together with 15 c.c. of benzene, after which oxygen was passed into one of the tubes. After two days, 11 c.c. of oxygen had been absorbed; the yellow colour of the hydroxide had disappeared, and the liquid was filled with slender needles of the dibenzoate. The solution in the other tube was unchanged, except that it had deposited a mere trace of the needles, the formation of which was doubtless due to oxygen dissolved in the benzene employed.

The needles of the dibenzoate from benzene contain 1 mol. of benzene of crystallisation, but, owing to rapid efflorescence, an accurate determination could not be made. From alcohol it is deposited in transparent prisms containing 1 mol. of alcohol of crystallisation.

3·8246 lost 0·2465 at 100°. Alcohol = 6·44.

$C_{49}H_{40}N_2O_4,C_2H_5\cdot OH$ requires alcohol = 6·01 per cent.

As it was probable that the dibenzoate would readily part with its extra molecule of benzoic acid, we dissolved it in alcohol, added alcoholic ammonia, and then precipitated the organic substance by adding water. A colourless, crystalline powder separated; square, tabular crystals of the same substance were also deposited from the mother liquor on standing. It melted at 180°. A nitrogen determination, made with substance dried at 120°, gave figures agreeing with those required by the expected *dibenzyllophonium monobenzoate*,



$$\begin{array}{l} C_6H_5\cdot C\cdot N^{V}(O\cdot CO\cdot C_6H_5)(C_7H_7)_2 \\ \quad\;\, \| \\ C_6H_5\cdot C \text{—————————————} N \end{array} \!\!> C\cdot C_6H_5.$$

0·2843 gave 11·75 c.c. moist nitrogen at 8° and 741·5 mm. N = 4·87.

$C_{42}H_{34}N_2O_2$ requires N = 4·68 per cent.

Dibenzyllophonium Nitrate.—This compound was incidentally obtained in the determination of chlorine in dibenzyllophonium chloride. The chlorine was precipitated from an alcoholic solution of the chloride with silver nitrate. The filtrate, on standing, deposited magnificent, lustrous crystals of rhombohedral habit, melting with decomposition and evolution of gas at 208°. They left no residue on ignition. This substance, which was obviously the nitrate formed by double decomposition, was recrystallised, and its percentage of nitrogen determined.

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0·1896 gave 12·0 c.c. moist nitrogen at 7·5° and 760·5 mm. N = 7·66.
$C_{35}H_{29}N_2\cdot NO_3$ requires N = 7·79 per cent.

2. *Benzil and Ethylamine.*

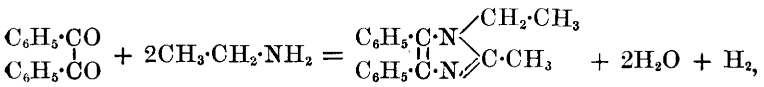
Four grams of benzil, 1·7 grams of ethylamine, dissolved in 5·5 c.c. of absolute alcohol, and 1·6 grams of finely-powdered zinc chloride were heated in a sealed tube for 5 hours at 120°. On cooling, the contents consisted of a dark pink liquid, with a white powder (zinc hydroxide).

The united product from several such tubes was dissolved in a smal quantity of alcohol with sufficient glacial acetic acid to dissolve the zinc hydroxide. Six volumes of ether were then added, which caused the separation of a viscous liquid. The supernatant ether was transferred to a separating globe, washed with water, preserving the aqueous liquid, and then shaken several times with very dilute hydrochloric acid. If the acid was too strong, a turbidity was occasioned, due to the insolubility of the hydrochloride of the new base in excess of hydrochloric acid; this disappeared on addition of water. The hydrochloric acid extracts were evaporated to dryness, and the syrupy residue treated with water, in which it all dissolved, excepting a small quantity of brown substance, which proved to be impure benzil. The clear aqueous solution was precipitated with ammonia and the liberated organic base extracted with ether. On evaporating the ether to a small bulk and allowing it to stand, the base crystallised with some difficulty. It was recrystallised from ether, and afterwards from light petroleum, which deposited it in large, lustrous prisms, melting constantly at 125·5°. A further quantity was obtained on addition of ammonia to the aqueous washings of the ether. The total yield from 24 grams of benzil was only about 2 grams. Analysis gave figures agreeing with the formula $C_{18}H_{18}N_2$.

0·1225 gave 0·3700 CO_2 and 0·0764 H_2O. C = 82·38; H = 6·93.
0·2343 ,, 20·6 c.c. moist nitrogen at 10·5° and 772·5 mm. N = 10·67.
$C_{18}H_{18}N_2$ requires C = 82·44; H = 6·87; N = 10·69 per cent.

The same compound is obtained when benzil and ethylamine are heated in alcoholic solution without the addition of zinc chloride but the yield is even less satisfactory.

The formation of the compound is represented by the equation



$$\begin{matrix}C_6H_5\cdot CO\\ |\\ C_6H_5\cdot CO\end{matrix} + 2CH_3\cdot CH_2\cdot NH_2 = \begin{matrix}C_6H_5\cdot C\cdot N\\ \|\\ C_6H_5\cdot C\cdot N\end{matrix}\!\!\begin{matrix}\diagup CH_2\cdot CH_3\\ \diagdown\\ \diagup\end{matrix}\!\! C\cdot CH_3 + 2H_2O + H_2,$$

and it has thus the constitution, as we shall prove by a separate synthesis, of *N-ethyl-diphenyl-μ-methyl-imidazole.*

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The hydrochloride is readily soluble both in water and in alcohol; but the salt is precipitated from the aqueous solution by excess of hydrochloric acid. On adding platinic chloride to the aqueous solution the platinichloride was deposited in well-formed, rhomboidal crystals. It was dried at 80° and analysed.

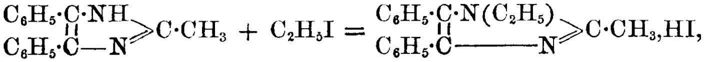
0·5581 gave 0·1168 platinum. Pt = 20·93.
$(C_{18}H_{18}N_2)_2H_2PtCl_6$ requires Pt = 20·84 per cent.

The viscous liquid, precipitated by ether in the treatment of the original product of the benzil ethylamine interaction, would contain, along with zinc chloride and zinc acetate, the zinc double salt of any quaternary chloride that had been formed. By dissolving it in water, removing the zinc with ammonium sulphide, evaporating the filtrate to dryness, extracting the residue with absolute alcohol, and again evaporating the alcoholic solution, a syrupy substance was obtained, which, from its reactions, was probably the quaternary chloride in question; but as we failed to obtain it in a crystallised form, we did not investigate it further. The difficulties which we afterwards experienced with the corresponding quaternary iodide, prepared by the union of the tertiary base with ethylic iodide, sufficiently explain our failure.

Synthesis of N-Ethyl-diphenyl-μ-methyl-imidazole from Diphenyl-μ-methyl-imidazole and Ethylic Iodide.—3 grams of diphenyl-μ-methyl-imidazole, prepared by the interaction of benzil, aldehyde and ammonia (Japp and Wynne, Trans., 1886, **49**, 464), were heated with excess of ethylic iodide in a sealed tube for 6 hours at 100°. The contents of the tube, consisting of a mass of brown crystals, were removed from the tube with alcohol, evaporated to dryness, dissolved in hot water, and the solution filtered. Ammonia precipitated an oily base, which, in contact with a crystal of the base $C_{18}H_{18}N_2$, obtained in the previous interaction, solidified. It was recrystallised from hot light petroleum, in which it all dissolved, excepting a small residue; this proved to be unchanged diphenyl-μ-methyl-imidazole. The solution deposited prisms melting at 125·5°, in every respect identical with those of the base $C_{18}H_{18}N_2$, with which formula a nitrogen determination also agreed.

0·1129 gave 10·3 c.c. moist nitrogen at 9° and 746·5 mm. N = 10·70.
$C_{18}H_{18}N_2$ requires N = 10·69 per cent.

It is formed according to the equation



$$\begin{array}{l}C_6H_5\cdot C\cdot NH\\ \quad\|\\ C_6H_5\cdot C—N\end{array}\!\!>C\cdot CH_3 + C_2H_5I = \begin{array}{l}C_6H_5\cdot C\cdot N(C_2H_5)\\ \quad\|\\ C_6H_5\cdot C\text{———}N\end{array}\!\!>C\cdot CH_3,HI,$$

thus proving it to be N-ethyl-diphenyl-μ-methyl-imidazole.

N-Diethyl-diphenyl-μ-methyl-imidazolonium Iodide.—This compound

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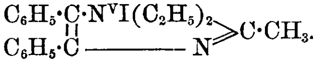
was prepared in order to obtain fresh proof of the tertiary nature of the base $C_{18}H_{18}N_2$.

One gram of the base $C_{18}H_{18}N_2$ was heated with excess of ethylic iodide in a sealed tube at 100—110° for four hours. The tube contained clear, well-shaped crystals of the new compound; these were removed with alcohol, and the solution evaporated to dryness. It was found impossible to obtain the compound in a crystallised form from any solvent. It was dissolved in water, in which it is only sparingly soluble, and the filtered solution was allowed to evaporate over sulphuric acid in a vacuum desiccator. It separated as an oil. When the water was all gone, this oil was heated on the water bath, and stirred with a glass rod, which had the desired effect of making it assume a crystalline form. Although the crystals melted as high as 163°, mere contact with ether, in which they are practically insoluble, caused them to liquefy. For analysis they were dried at 120—130°.

1·0351 gave 0·5816 AgI. I = 30·35.

$C_{20}H_{23}N_2I$ requires I = 30·32 per cent.

Its constitution is represented by the formula



$$\begin{array}{l} C_6H_5\cdot C\cdot N^{V}I(C_2H_5)_2 \\ \quad\;\; \| \\ C_6H_5\cdot C \text{———————} N \end{array} \!\!>\! C\cdot CH_3.$$

3. *Phenanthraquinone and Methylamine.*

Eight grams of phenanthraquinone and 2·5 grams of methylamine, the latter being dissolved in 12 grams of absolute alcohol, were heated in a sealed tube for six hours at 90—95°. The tube, on cooling, contained a brown liquid with a small quantity of a brown solid. The whole was treated with hot alcohol, which dissolved everything except about two grams of solid substance. The alcoholic solution, on standing, deposited a small quantity of a yellowish-brown substance, which was removed by filtration, evidently the sparingly soluble compound described by Zincke and Hof (*loc. cit.*); but we did not trouble further about this compound, as it was the readily soluble base which we wished to examine. To the alcoholic filtrate hydrochloric acid was added; the liquid was evaporated to a small bulk, and then extracted with water. On adding ammonia to the aqueous extract, the organic base was precipitated as a brown powder. Following Zincke and Hof's directions, we recrystallised the compound from alcohol, but, finding that this did not readily remove the colour, we employed light petroleum as a solvent, and thus obtained the base in colourless needles melting at 188° (185—186°, according to Zincke and Hof). Analysis gave figures pointing to the formula $C_{16}H_{12}N_2$, which contains two atoms of hydrogen fewer than that given by Zincke and Hof.

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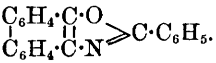
0·1373 gave 0·4165 CO_2 and 0·0639 H_2O; C = 82·73; H = 5·17.
0·1375 „ 0·4174 CO_2 and 0·0659 H_2O; C = 82·79; H = 5·33.
0·1292 „ 13·15 c.c. moist nitrogen at 9° and 752·5 mm. N = 12·12.
$C_{16}H_{12}N_2$ requires C = 82·76; H = 5·17; N = 12·07 per cent.

Zincke and Hof's formula, $C_{16}H_{14}N_2$, on the other hand, requires C = 82·05; H = 5·98; N = 11·97 per cent. As already mentioned, no analyses are given in their paper.

The constitution of an *N-methyl-diphenylene-imidazole*, which we incline to assign to this compound, is given in the Introduction to the present paper. Since, according to this view, the compound is a tertiary amine, it ought to combine with alkyl haloïds. We accordingly heated it with methylic iodide and methylic alcohol in a sealed tube, and obtained a compound which crystallised from its aqueous solution in prisms, and was not precipitated by ammonia; but as at each recrystallisation this substance became in part reddish-brown and insoluble, apparently from oxidation, we did not examine it further.

4. *Phenanthraquinone and Benzylamine.*

Four grams of phenanthraquinone were rubbed in a mortar with 1·5 gram of zinc chloride. The mixture, which was of a dark reddish-brown colour, owing to the formation of the double compound of these two substances, was transferred to a large boiling tube, and 4 grams of benzylamine were added. Immediately there was an effervescence, with evolution of heat, and the colour changed to dark blue. The mixture was heated on the water bath, but as no change was observed, it was transferred to an oil bath, and the temperature gradually raised, first to 120° and ultimately to 150°. The effervescence increased, lasting for a few minutes, and ammonia was given off. The heating was continued for half an hour. The mass on cooling was hard, and of a dull yellow colour. It was powdered and then extracted with boiling alcohol, which dissolved but a small proportion. The alcoholic solution, on standing, deposited needle-shaped crystals with a silky lustre; these were recrystallised from benzene, when they melted at 197°. From the melting point, appearance, ready solubility in benzene, and sparing solubility in alcohol or glacial acetic acid, it was evidently identical with *diphenylene-μ-phenyloxazole*,



$$\begin{array}{l} C_6H_4\cdot C\cdot O \\ \,|\qquad \| \\ C_6H_4\cdot C\cdot N \end{array}\!\!>C\cdot C_6H_5.$$

The latter compound, it is true, melts at 202°; but this melting point can be observed only with colourless substance, and after repeated recrystallisation; whereas the present specimen had a yellowish

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tinge, and the quantity was insufficient for further purification. It was, therefore, identified by careful comparison with a specimen of diphenylene-μ-phenyloxazole prepared from phenanthraquinone, benzaldehyde, and ammonia. Except as regards the slight, yellowish tinge, and the fact that it melted 2° lower, it was indistinguishable from this specimen. Finally, a nitrogen determination gave a value agreeing with that required by the formula.

0·1988 gave 8 c.c. moist nitrogen at 8° and 742 mm.; N = 4·74.
$C_{21}H_{13}NO$ requires N = 4·74 per cent.

The substance which remained after extracting with boiling alcohol was found to be insoluble in the ordinary organic solvents of low boiling point. It could be recrystallised, however, from boiling aniline, from which it was deposited in microscopic, brownish, rectangular prisms, with a bronze lustre. It was twice crystallised from this solvent, washed with alcohol, and dried for analysis. It did not melt below 300°, and could not be sublimed. When dissolved in cold concentrated sulphuric acid, it gave a very faint bluish colour; but the liquid, on warming on the water bath, became of an intense blue colour, and this solution, when diluted with water, dyed silk greenish-blue; the colour fading, however, in a few days. Two combustions of different preparations, together with a nitrogen determination, were made; but the figures were not very concordant: C = 87·28—88·00; H = 4·58—5·01; N = 3·94. The nearest to this is the formula $C_{28}H_{17}NO$, which requires C = 87·72; H = 4·44; N = 3·66 per cent. The substance was difficult to burn.

On adding alcohol to the aniline mother liquor from the first of the foregoing crystallisations, microscopic, yellowish, rhomboidal plates were precipitated. These proved to be tetraphenyleneazine, $C_{28}H_{16}N_2$. It dissolved in cold concentrated sulphuric acid, with the characteristic, intense blue colour, which disappears on addition of water. So far as we are aware, tetraphenyleneazine has not hitherto, on account of its sparing solubility, been obtained crystallised from any solvent; it has been usual to purify it by sublimation.

Other experiments were made on the interaction of phenanthraquinone and benzylamine without the addition of zinc chloride; but the same products were obtained as in the previous case.

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