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XLIII.—Condensation of Benzil with Ethylic Acetoacetate.

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THE following investigation was undertaken in the hope of throwing light on the constitution of the compounds obtained by the condensation of benzil with acetone, especially on that of anhydracetonebenzil. This hope has not been fulfilled; but as we believe that we have in the meantime attained our object by the more direct method of a detailed study of the reactions of anhydracetonebenzil itself, we do not intend to carry our examination of the present condensation further, especially as, owing to the high molecular weight of the compounds formed, and the consequent uncertainty in interpreting the analytical data, the work is of great difficulty. We therefore content ourselves with placing on record the results obtained.

Action of Sodium Ethoxide on a Mixture of Benzil and Ethylic Acetoacetate.—Eight grams of sodium were dissolved in about 100 grams of absolute alcohol; the solution was cooled; 40 grams of ethylic acetoacetate and 70 grams of benzil were added; and the whole was warmed on the water bath until the benzil had dissolved, after which the flask was removed from the water bath, and allowed to stand over night. A crystalline substance was deposited, which proved to be a sodium compound of the new condensation product, and contained alcohol of crystallisation; it had the formula $C_{34}H_{27}NaO_{67}C_{2}H_{6}O$. This substance was separated by filtration, and washed with cold alcohol. Addition of alcohol to the mother liquor produced a further deposit of the substance; this was treated in the same way. The second mother liquor thus obtained gave, on dilution with water, a third portion of the substance in a less pure condition.

This sodium compound, like the metallic derivatives of ethylic acetoacetate, is readily soluble in benzene. The first two crops of crystals were therefore united and dissolved in benzene, after which glacial acetic acid was added until the liquid showed a slight acid reaction. Sodium acetate separated, and was removed by filtration. The clear solution was diluted with light petroleum; on standing, the liquid very slowly deposited nearly the whole of the new compound in crystalline crusts. The yield was 42 grams, whilst a further quantity was obtained from the third crop of sodium compound. Thus purified, it contains benzene of crystallisation, and the crystals effloresce on exposure to air. It may be purified by recrystallisation, either from hot alcohol or from a mixture of ethylic acetate and light petroleum; both solvents deposit it in colourless, flat needles or

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prisms, with bevelled edges. It melts with decomposition at $210-211^{\circ}$. It has the formula $C_{34}H_{28}O_6$, and is formed from benzil and ethylic acetoacetate, according to the equation

$$2C_{14}H_{10}O_2 + C_6H_{10}O_3 = C_{34}H_{28}O_6 + H_2O.$$

It may, therefore, be provisionally named *ethylic anhydrodibenzilacetoacetate*. Analysis of the air-dried substance gave results agreeing with the foregoing formula.

The substance is somewhat difficult to burn; but we were led unnecessarily to doubt the accuracy of some of our first combustions by noticing the formation of a permanent black deposit in the combustion tube above the oxide of copper just in the neighbourhood of the substance. This we at first took to be unburnt carbon; but it proved to be oxide of copper. The phenomenon was doubtless due to the regeneration of ethylic acetoacetate, and the formation of its volatil copper compound, which was then decomposed in contact with the hotter portions of the tube. The formation and volatilisation of ethylic cupracetoacetate under such conditions may be readily shown, as we found, by heating in a test-tube a little finely powdered copper oxide, moistened with ethylic acetoacetate; on setting fire to the vapour at the mouth of the tube it burns with a green flame.

The original sodium compound, $C_{34}H_{27}NaO_6$, C_2H_6O , does not readily give good figures for sodium and alcohol, owing to the fact that it is very difficult to expel the whole of the alcohol of crystallisation without decomposing the remaining compound. Loss on heating at 110° : 8.21 to 9.03 per cent.; calculated for 1 mol. C_2H_6O : 7.67 per cent. Na in resulting substance: found 3.99 to 4.55 per cent.; calculated 4.15 per cent.

This sodium compound is, as already mentioned, very soluble in benzene. If a strong benzene solution is allowed to stand for two or three weeks in a corked flask, large, transparent crystals, containing benzene of crystallisation are slowly deposited. These are sparingly soluble in benzene; but on exposure to air, or when gently heated, they effloresce, and the effloresced substance again dissolves readily in benzene.

Although ethylic anhydrodibenzilacetoacetate, as some of its other reactions show, undoubtedly contains the carbethoxyl group, it was not found possible to hydrolyse it by means of alkali to the corresponding acid, owing to the ease with which it is decomposed with regeneration of benzil.

No acetyl derivative was obtained by boiling ethylic anhydrodibenzilacetoacetate with acetic anhydride for one hour.

The substance was also heated alone at 150-160° in a flask, previously exhausted by a Sprengel mercury pump. Carbon dioxide was given off, mixed, towards the end of the operation, with a gas which was not absorbed by caustic potash. After the evolution of gas had ceased, the residue in the flask was dissolved in benzene. The solution deposited benzil. No other compound could be isolated from this residue.

Phenylhydrazine does not act on the compound in boiling alcoholic solution. At a higher temperature the dihydrazone of benzil is obtained.

Action of Ethylic Alcohol and Sulphuric acid on Ethylic Anhydrodibenzilacetoacetate.---Ten grams of ethylic anhydrodibenzilacetoacetate were boiled for five hours with a mixture of 200 c.c. of absolute alcohol and 10 drops of concentrated sulphuric acid, using a reflux condenser. The substance was precipitated by the addition of water, and purified by recrystallisation from boiling alcohol. It formed slender prisms or needles melting at 197°. (Yield: 5.5 grams of pure substance.) In purifying various preparations of this substance, it was frequently noticed that the mother liquors from the needles melting at 197° deposited, on standing, other needles, very similar to these in appearance, but melting at 178°. On recrystallising the latter substance from alcohol, the melting point at once rose to 197°. The compound thus appears to be dimorphous. Analysis of the substance dried at 100° showed that a hydrogen atom of ethylic anhydrodibenzilacetoacetate had been replaced by ethyl

 $C_{34}H_{28}O_6 + C_2H_6O = C_{34}H_{27}(C_2H_5)O_6 + H_2O_7$

yielding ethylic ethylanhydrodibenzilacetoacetate.

0.1700 gave 0.4791 CO₂ and 0.0893 H₂O. C = 76.86; H = 5.84. 0.2033 0.5742 CO_2 , $0.1056 \text{ H}_2\text{O}$. C = 77.02; H = 5.77. $C_{36}H_{32}O_6$ requires C = 77.14; H = 5.71 per cent.

An attempt was made to prepare this compound by heating ethylic anhydrodibenzilsodacetoacetate in benzene solution in a sealed tube with ethylic iodide. A separation of sodium iodide occurred, showing that an interaction had taken place; but the benzene solution, on evaporation, yielded a large quantity of benzil. A very minute quantity of a substance crystallising in tufts of needles was also formed, quite insufficient for further investigation.

It is, therefore, probable that sodium and ethyl replace different hydrogen atoms of the condensation compound.

Of the two ethyl groups contained in the molecule of ethylic ethylanhydrodibenzilacetoacetate, that which was already present in by hydrolysis with caustic alkali. Ethylanhydrodibenzilacetoaceticacid.-Ethylic ethylanhydrodibenzilacetoacetate was heated with alcoholic potash for half an hour on the water bath. On standing over night, the solution deposited prismatic crystals of a potassium salt. (In a subsequent preparation it was found that the addition of more alcohol facilitated the crystal-The crystals were separated by filtration lisation of this salt.) through a platinum cone, and washed with alcohol. They were practically insoluble both in alcohol and in water, but dissolved on warming with water containing a little alcohol. The organic acid was precipitated by dilute sulphuric acid, and purified by recrystallisation from hot benzene. The benzene solution deposited the substance in a form which appeared to the eye amorphous, but under the microscope was seen to consist of minute matted needles. \mathbf{It} melted constantly at 216°. 5.5 grams of ester yielded 3.5 grams of acid. Analysis of the substance dried at 100° gave figures agreeing with the expected formula of ethylanhydrodibenzilacetoacetic acid, $C_{32}H_{23}(C_2H_5)O_6.$

0.2348 gave 0.6603 CO₂ and 0.1130 H₂O. C = 76 69; H = 5.34. 0.1453 , 0.4083 CO₂ , 0.0708 H₂O. C = 76.63; H = 5.41. $C_{34}H_{28}O_6$ requires C = 76.69; H = 5.26 per cent.

It is isomeric with the condensation compound.

The silver salt was obtained by precipitating a solution of the ammonium salt in dilute alcohol with an aqueous solution of silver nitrate. It formed a white precipitate, which showed a tendency to become dark coloured. It was dried in a vacuum desiccator.

0.2918 gave, on ignition, 0.0500 Ag. Ag = 17.13. $C_{34}H_{27}O_{6}Ag$ requires Ag = 16.90 per cent.

The barium salt was obtained in a similar manner, precipitating with barium chloride. It was recrystallised from a mixture of water with rather more than its volume of alcohol, and was thus obtained in small prisms. For analysis it was dried at 100° .

0.3614 gave 0.0694 BaSO₄. Ba = 11.29.

 $(C_{34}H_{27}O_6)_2$ Ba requires Ba = 11.43 per cent.

In order to prove that the ethyl group, which is removed during the hydrolysis of ethylic ethylanhydrodibenzilacetoacetate to the acid is, as already stated, that which was already present in the condensation compound, we next prepared ethylic isobutylanhydrodibenzilacetoacetate, and subjected it to hydrolysis. Only the ethyl group

was removed, and isobutylanhydrodibenzilacetoacetic acid was formed.

Action of Isobutylic Alcohol and Sulphuric acid on Ethylic Anhydrodibenzilacetoacetate.—Ten grams of ethylic anhydrodibenzilacetoacetate were boiled with a mixture of 200 grams of isobutylic alcohol and 50 drops of concentrated sulphuric acid for five hours. About half the liquid was then distilled off, and the remainder poured into water, which occasioned the separation of a viscid mass. By repeated recrystallisation from a mixture of benzene and light petroleum the substance was obtained in minute needles melting constantly at 192°. Analysis of the compound, dried at 100°, gave figures agreeing with those required for ethylic isobutylanhydrodibenzilacetoacetate,

$C_{34}H_{27}(C_4H_9)O_6.$

In a subsequent preparation of this compound we obtained a small quantity of a substance identical in appearance with the foregoing, but melting constantly at 202°. As it gave practically the same figures on analysis (Found : C = 77.57; H = 6.69 per cent.), the hydrogen alone being somewhat higher, we assumed that it was the same compound, but in a purer condition, and in a preliminary note (Proc., 1895, 147) we gave 202° as the melting point of the compound. It is possible, however, that this second substance may be *isobutylic isobutylanhydrodibenzilacetoacetate*, $C_{40}H_{40}O_6$ (Calculated : C = 77.92; H = 6.49 per cent.), formed from the ethylic ester by the displacement of ethyl by isobutyl under the influence of the sulphuric acid. We must, therefore, leave the question of the correct melting point open.

Isobutylanhydrodibenzilacetoacetic acid.—The hydrolysis of ethylic isobutylanhydrodibenzilacetoacetate (m. p. 192°) was carried out exactly as in the case of the ester already described, except that, as the potassium salt did not separate so readily in the present case, the solution in alcoholic potash was diluted with water, warmed until any salt redissolved, and precipitated with dilute sulphuric acid. The new acid was somewhat difficult to purify. From its solution in benzene it was deposited in dark-coloured crystals. The best result was obtained by dissolving the acid in boiling ethylic acetate and diluting with light petroleum. The substance was deposited in colourless slender needles melting constantly at 237°. Analysis of the compound, dried in a vacuum desiccator, gave figures agreeing with the formula of *isobutylanhydrodibenzilacetoacetic acid*,

 $C_{32}H_{23}(C_4H_9)O_6.$

0.1634 gave 0.4613 CO₂ and 0.0863 H₂O. C = 70.99; H = 5.84. 0.1741 , 0.4928 CO₂ , 0.0907 H₂O. C = 77.19; H = 5.78. $C_{35}H_{32}O_6$ requires C = 77.14; H = 5.71 per cent.

The silver salt and the barium salt were prepared like the corresponding salts of the ethyl acid.

The silver salt was obtained as a white precipitate. It was dried in a vacuum desiccator.

0.2908 gave, on ignition, 0.0462 Ag. Ag = 15.88.

 $C_{36}H_{31}O_6Ag$ requires Ag = 16.19 per cent.

The barium salt was recrystallised from dilute alcohol, from which it was deposited in slender needles. It was dried at 100°.

0.4362 gave 0.0792 BaSO₄. Ba = 10.68.

 $(C_{35}H_{31}O_6)_2$ Ba requires Ba = 10.92 per cent.

Oxidation of Ethylic Anhydrodibenzilacetoacetate.-Ten grams of the condensation compound were dissolved in glacial acetic acid, and to the warm solution 10 grams of chromium trioxide, also dissolved in glacial acetic acid, were gradually added. Considerable heat was evolved, and the reaction was completed without further warming. Addition of water precipitated an organic substance, which was separated by filtration and treated with a solution of sodium carbonate to remove acids; the residue was apparently chiefly unchanged The acids were reprecipitated with sulphuric acid and substance. treated with a little ether to remove benzoic acid; the organic acid which remained was dissolved in ethylic acetate, and light petroleum added; the solution deposited slender needles melting constantly at 200° with evolution of gas. The yield of acid in different preparations was not more than from 1 to 1.5 gram from 10 grams of the condensation compound. Analysis gave figures which led to the formula C₂₂H₁₆O₄.

0.1492 gave 0.4208 CO₂ and 0.0640 H₂O. C = 76.92; H = 4.76. 0.1932 , 0.5456 CO₂ , 0.0794 H₂O. C = 77.02; H = 4.56. $C_{22}H_{16}O_4$ requires C = 76.74; H = 4.65 per cent.

The silver salt was prepared by precipitating an aqueous solution of the ammonium salt with silver nitrate. It formed a white powder which did not darken appreciably at 100°.

0.4437 gave, on ignition, 0.1028 Ag. Ag = 23.70. $C_{22}H_{15}O_4Ag$ requires Ag = 23.95 per cent.

We give reasons later on for regarding this acid as *phenyldibenzoyl*-acetic acid.

Action of Heat on Phenyldibenzoylacetic acid.—In order to ascertain the nature of the decomposition occurring at the melting point of

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this acid, 5 grams of the substance were introduced into an Anschütz distilling flask (with receiver fused on), the flask was exhausted by means of a Sprengel mercury pump, and then heated to 200°. At this temperature a gas was evolved, which was found to be pure carbon dioxide; the fused acid assumed a deep violet colour. As soon as the evolution of gas had ceased the residue was distilled under reduced pressure; it passed over at $300-305^{\circ}$ under a pressure of about 15 mm. The distillate, which formed a clear brown resin, was dissolved in hot alcohol; from a dilute solution it was deposited in flat needles melting constantly at $119-120^{\circ}$. The yield in the foregoing experiment was only 1.5 gram. The substance is insoluble in aqueous caustic alkalis. Analysis gave figures agreeing best with the formula $C_{21}H_{16}O_2$, the compound having been formed from the acid according to the equation

$$C_{22}H_{16}O_4 = C_{21}H_{16}O_2 + CO_2.$$

0.1250 gave 0.3856 CO₂ and 0.0574 H₂O. C = 84.13; H = 5.10. 0.1024 , 0.3162 CO₂ , 0.0492 H₂O. C = 84.20; H = 5.33. C₂₁H₁₆O₂ requires C = 84.00; H = 5.33 per cent.

The following formulæ might express the constitution of the acid and its product of decomposition.

| C ₆ H₅·ÇO | | C₅H₅∙ÇO | |
|-----------------------------|---------------|---------------------|----|
| C₄H₅∙Ċ∙COOH | and | C₅H₅∙ĊH | |
| C_6H_5 CO | | С₅Н₅∙СО | |
| Phenyldibenzoylacetic acid. | \mathbf{Ph} | enyldibenzoylmethan | e. |

The following considerations appear to favour the foregoing formula for the acid.

The condensation compound, $C_{34}H_{28}O_6$, being formed according to the equation

$$\begin{array}{rl} 2\mathrm{C}_{14}\mathrm{H}_{10}\mathrm{O}_2 \,+\, \mathrm{C}_6\mathrm{H}_{10}\mathrm{O}_3 \,=\, \mathrm{C}_{34}\mathrm{H}_{28}\mathrm{O}_6 \,+\, \mathrm{H}_2\mathrm{O},\\ & \text{Benzil.} & \text{Ethylic aceto-}\\ & \text{acetate.} \end{array}$$

must contain in its molecule four C_6H_5 C groups derived from benzil. In the oxidation of the compound each C_6H_5 C group, if removed, must be removed as a whole. In the formation of an acid of the formula $C_{22}H_{16}O_4$, one C_6H_5 C group has been so removed. The three which remain account for $C_{21}H_{15}$, that is, for all the carbon and hydrogen in the molecule of the acid except the one atom of each of these elements required for the carboxyl group. This carbon atom of the carboxyl group is all that remains of the molecule of ethylic acetoacetate. The foregoing mode of formulating the acid as phenyldibenzoylacetic acid seems, therefore, to be the most natural. Indeed, the only alternative constitution, so far as we can see, would be C_6H_5 ·CO·O·C(C_6H_5):C(C_6H_5)·COOH, which is the formula of a benzoate derived from the enolic form of deoxybenzoïncarboxylic acid. Such a compound would, however, be readily hydrolysed to benzoic acid and deoxybenzoïncarboxylic acid, the latter thereafter breaking up into deoxybenzoïn and carbon dioxide; but the present acid, when heated with a solution of caustic alkali, is stable. Moreover, it would be necessary to assume the existence of this complex in the molecule of the condensation compound—an assumption quite out of keeping with the ease with which the latter compound regenerates benzil.

It might be objected that the acid is too stable to have the constitution of a β -ketonic acid. W. H. Perkin, jun., has, however, shown that, although benzoylacetic acid, when heated to its melting point (104°), parts with carbon dioxide, dibenzoylacetic acid, on the other hand, melts at 109° without decomposition, and may even, in small quantities, be distilled undecomposed. The introduction of a phenyl group into the molecule of dibenzoylacetic acid would in all probability give it the stability of the acid under consideration.

From the formula of the acid, that of the diketone follows as a matter of course.

The chief objection to this mode of formulating these compounds lies in the fact that the supposed diketone does not interact with phenylhydrazine even at the boiling point of the latter, whereas it might have been expected to yield with it tetraphenylpyrazole, just as Knorr (Annalen, 1894, **279**, 235) has prepared tetramethylpyrazole by the interaction of methylhydrazine with methylacetylacetone (methyldiacetylmethane). It may be, however, that there are stereochemical reasons for the non-existence of a tetraphenylpyrazole, just as there is a tetramethylmethane, but no tetraphenylmethane.

The insolubility of the diketone in aqueous caustic alkalis would indicate that it has no tendency to assume the enolic form which is necessary to the formation of a pyrazole. But of course it might interact with phenylhydrazine without forming a pyrazole.

Attempts which we made to introduce a benzoyl group into the molecule of deoxybenzoïn, so as to synthesise a compound of the formula of the foregoing diketone, proved unsuccessful.

If the foregoing formulæ are correct, it follows that, in the formation of the condensation compound, the two benzil complexes become united to one another by carbon bonds, and, further, that the acetoacetic group enters into similar union with the resulting dibenzil complex.

Reduction of Ethylic Anhydrodibenzilacetoacetate and its Ethyl and Isobutyl Derivatives with Hydriodic acid.—Finely powdered ethylic anhydrodibenzilacetoacetate was boiled for about three minutes with

excess of fuming hydriodic acid, shaking the flask during the whole operation. The substance fused. Water was then added, the liquid extracted with ether, and the ethereal extract was shaken with a dilute solution of sulphur dioxide to remove iodine, then with water, and finally with a solution of sodium carbonate. The latter solution was found not to have taken up any organic acid. During the process a portion of the reduction product separated from the ether in a crystalline form. The ether, on evaporation, left a gummy mass; this was dissolved in ethylic acetate, and light petroleum added; the liquid deposited lustrous, short prisms, which, after recrystallisation, melted without decomposition constantly at 187— 188°. Analysis of substance dried at 50° gave the following figures.

0.1736 gave 0.5732 CO₂ and 0.0903 H₂O. C = 90.05; H = 5.77. 0.1545 , 0.5096 CO₂ , 0.0823 H₂O. C = 89.94; H = 5.91. $C_{28}H_{22}O$ requires C = 89.84; H = 5.88 per cent.

In our previous note on this subject (Proc., 1895, 147) we deduced from these results the formula $C_{31}H_{24}O$ (calculated, C = 90.29; H =5.83 per cent.), assuming that, along with the reduction, there had been an elimination of the carbethoxyl group from the condensation compound. Since then, however, we have reduced the ethyl and isobutyl derivatives of the condensation compound, both of which also yield the foregoing substance melting at 187—188°; but along with this we obtained from the ethyl derivative, by boiling for a short time with the hydriodic acid, a compound $C_{28}H_{22}O_2$ (m. p. 221°) as an intermediate product. The higher proportion of oxygen in this compound enables its formula to be calculated with greater certainty, and as it is converted by longer boiling with the hydriodic acid into the compound of m. p. 187—188°, we must assume that the latter is its reduction product and has the formula $C_{28}H_{22}O$.

The foregoing illustrates the difficulty of dealing with some of these compounds. In the case of the compound containing only one atom of oxygen, analysis alone is incompetent to decide the formula. We did not attempt a Raoult determination, as the method is not sufficiently accurate for the present purpose.

Neither acetic anhydride at its boiling point, nor phenylhydrazine in alcoholic solution at 150°, had any action on the compound $C_{23}H_{22}O_2$.

The reduction in the case of the ethyl and isobutyl derivatives was carried out as described in the case of ethylic anhydrodibenzilacetoacetate, and the mode of purification of the product was also the same. In the case of the ethyl derivative we found, as just stated, that by boiling for a short time (under five minutes) with the hydriodic acid, a compound was obtained crystallising in needles melting

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at 221°; whereas if the substance was boiled for longer (seven minutes) the compound $C_{28}H_{22}O$, crystallising in short prisms melting at 187–188° was formed. The compound melting at 221° was purified by crystallisation, first from ethylic acetate, afterwards from glacial acetic acid. Analysis gave figures agreeing with the formula $C_{28}H_{22}O_2$.

0.1215 gave 0.3835 CO₂ and 0.0643 H₂O. C = 86.08; H = 5.79. 0.1388 , 0.4384 CO₂ , 0.0707 H₂O. C = 86.14; H = 5.66. C₂₈H₂₂O₂ requires C = 86.15; H = 5.64 per cent.

The isobutyl derivative gave as chief product of reduction the compound $C_{28}H_{22}O$ (m. p. 187—181°); but along with it another crystalline substance melting at 155°. The quantity was too small for further investigation; but the substance appeared to be identical with a compound melting at 155—159° obtained in the reduction of anhydracetonedibenzil (see following section).

If the formulæ containing 28 atoms of carbon correctly express the composition of the reduction compounds, it is evident that the hydriodic acid completely removes the acetoacetic group from the condensation compound and its derivatives, only the dibenzil complex remaining.

Reduction of Anhydracetonedibenzil with Hydriodic acid.—The mode of formation of ethylic anhydrodibenzilacetoacetate is strictly analogous to that of anhydracetonedibenzil, which, as Japp and Miller have shown (Trans., 1885, 47, 34), is formed from benzil and acetone according to the equation

$$2C_{14}H_{10}O_2 + C_3H_6O = C_{31}H_{24}O_4 + H_2O.$$

It thus appeared probable that ethylic anhydrodibenzilacetoacetate was the carbethoxyl derivative of anhydracetonedibenzil. We therefore reduced the latter compound with hydriodic acid, in order to ascertain whether it would yield the same products as the former.

The reduction was carried out as already described. A product was obtained which was deposited from a mixture of ethylic acetate and light petroleum in two forms; small, lustrons prisms melting at $187-188^{\circ}$, identical with the reduction product of ethylic anhydro-dibenzilacetoacetate; and larger crystals, of pyramidal habit, melting at $155-159^{\circ}$. The two forms were separated mechanically and then further purified by recrystallisation. The melting points were unchanged. Both substances gave figures agreeing with the formula $C_{28}H_{22}O$.

Small prisms (m. p. 187-188°).

0.2281 gave 0.7490 CO₂ and 0.1193 H₂O. C = 89.55; H = 5.81. C₂₈H₂₂O requires C = 89.84; H = 5.88 per cent.

Pyramids (m. p. 155-159°).

0.1428 gave 0.4706 CO₂ and 0.0758 H₂O. C = 89.88; H = 5.89. C₂₈H₂₂O requires C = 89.84; H = 5.88 per cent.

We also oxidised anhydracetonedibenzil with chromium trioxide in acetic acid solution, in order to ascertain whether phenyldibenzoylacetic acid was formed, but did not succeed in identifying this substance among the products of oxidation.

Constitution of Ethylic Anhydrodibenzilacetoacetate.—It is perhaps premature, on the strength of the foregoing very imperfect study of this substance, to attempt to assign to it a constitutional formula; and the following must therefore be regarded as merely a provisional expression which, as far as it goes, appears to us to account for the reactions here described.

That two molecules of benzil interact with one of ethylic acetoacetate must be ascribed to the fact that the latter compound contains two groups—methylene and methyl—both of which, owing to their mode of combination, are capable of undergoing condensation with the carbonyl groups of benzil. If we assume that the first stage of the interaction is the double occurrence of an aldol condensation, we should have, as an intermediate product,

 $\begin{array}{ccc} C_{e}H_{5} \cdot CO & COOC_{2}H_{5} \\ C_{e}H_{5} \cdot C(OH) \cdot CH \cdot CO \\ C_{e}H_{5} \cdot C(OH) & - CH_{2} \\ C_{e}H_{5} \cdot CO \end{array}$

This hypothetical intermediate compound must then part with a molecule of water, and at the same time the two benzil residues must become united by means of carbon bonds, so as to account for the formation of phenyldibenzoylacetic acid on oxidation. To satisfy these conditions, we must assume the occurrence of some such rearrangement as the following:



Ethylic anhydrodibenzilacetoacetate.

The portion of the formula enclosed by the dotted line represents that part of the molecule which, in the process of oxidation, forms phenyldibenzoylacetic acid. In this process, the lower benzoyl group in the formula is removed in preference to the upper, because it is attached to a carbon atom which is already partially oxidised.

The sodium derivative on the one hand, and the alkyl derivatives

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on the other, in which, as has been shown, metal and alkyl replace different hydrogen atoms of the condensation compound, are to be regarded as derived from two distinct enolic forms of the foregoing.

| $C_6H_5 \cdot \dot{C} - \dot{C} = \dot{C}(ONa) \qquad C_6H_5 \cdot \dot{C} - \dot{C}H \cdot C(OC_2H)$ | I₅) |
|---|------------|
| $C_6H_5 \cdot \dot{C} - O - \dot{C}H_2 $ $C_6H_5 \cdot \dot{C} - O - \dot{C}H$ | |
| $C_6H_5 \cdot \dot{C}O$ $C_6H_5 \cdot \dot{C}O$ | |
| Ethylic anhydrodibenzil- sodacetoacetate. Ethylic ethylanhydrodibe acetoacetate. | nzil- |

The sodium compound being formulated on the analogy of ethylic sodacetoacetate; the ethyl derivative on a different type. These formulæ would explain why the ethyl derivative cannot be obtained by the action of ethylic iodide on the sodium compound; also why the alkylated acids are stable, and anhydrodibenzilacetoacetic acid itself so unstable that it could not be obtained from its ester; the reason being that the latter acid is a β -ketonic acid, whilst the alkylated acids are substituted unsaturated acids.

An objection might be raised to the foregoing formula for ethylic anhydrodibenzilacetoacetate on the ground that in a compound of this constitution, the acetoacetic group should not be removable by hydriodic acid. A precisely similar separation of carbon from carbon in the course of a hydriodic acid reduction has, however, been observed by Japp and Wadsworth (Trans., 1890, **57**, 971) in the case of paradesylphenol, $\begin{array}{c} C_6H_5 \cdot CH \cdot C_8H_4 \cdot OH\\ C_6H_5 \cdot CO\end{array}$, where a separation of the

desyl group from the nucleus of the phenol occurs. Moreover, as the carbon atom of the carboxyl group of the phenyldibenzoylacetic acid obtained from ethylic anhydrodibenzilacetoacetate by oxidation, is furnished, as we have already shown, by the ethylic acetoacetate, the existence of this carbon linkage must be granted.

The constitutional formula of anhydracetonedibenzil, $C_{31}H_{24}O_4$, may be derived from that of ethylic anhydrodibenzilacetoacetate by substituting hydrogen for the carbethoxyl group.

In conclusion we may call attention to the totally different character of the interaction of ethylic acetoacetate with benzil and phenanthraquinone respectively. In the latter case, one molecule of each substance takes part in the condensation.

| $C_{14}H_8O_2$ | + | $C_6H_{10}O_3$ | = | $\mathrm{C}_{20}\mathrm{H}_{16}\mathrm{O}_4$ | + | H_2O | | |
|----------------|---|----------------|-----------------|--|--------|--------|--|--|
| Phenanthra- | | Ethylic | Ethylic phenan- | | | | | |
| quinone. | | acetoacetate. | \mathbf{t} | iroxyleneacetoac | etate. | | | |

(Japp and Streatfeild, Trans., 1883, **43**, 27; Japp and Klingemann, Trans., 1891, **59**, 1). In fact, there are hardly any reactions in the

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whole range of organic chemistry more erratic than the condensations of the α -diketones with ketones and ketonic acids; it is hardly possible to say beforehand what course the reaction will take in any particular case.

The study of the condensation of benzil with ethylic acetoacetate was begun in 1888 by one of us in conjunction with Dr. Felix Klingemann, who prepared the condensation compound and its ethyl derivative; but, owing to pressure of other work, it was at that time postponed.

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