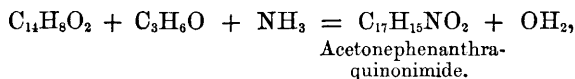


II.—On Additive and Condensation Compounds of Diketones with Ketones.

By FRANCIS R. JAPP, M.A., Ph.D., and N. H. J. MILLER, Ph.D.

Introduction.

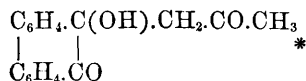
IN a former communication by Japp and Streatfeild (this Journal, 1882, Trans., 270), it was shown that phenanthraquinone, acetone, and ammonia react according to the equation—



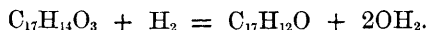
and that, when the compound thus obtained is treated with aqueous acids, it takes up water and parts with ammonia, yielding a compound of the formula $\text{C}_{17}\text{H}_{14}\text{O}_3$; this contains the elements of acetone and phenanthraquinone, and may, in fact, be obtained in small quantity by heating these two substances together. It may therefore receive, the name *acetonephenanthraquinone*. Owing to the ease with which, on heating, it was decomposed into acetone and phenanthraquinone, a

constitutional formula was assigned to it, in which the union of the two molecules of the generating compounds was represented as taking place by means of the oxygen-atoms.

A further study of the reactions of this compound has now shown that it possesses the constitution—



Thus when reduced with zinc-dust in acetic acid solution, it yields a compound of the formula $\text{C}_{17}\text{H}_{12}\text{O}$:—

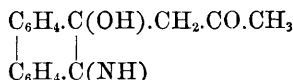


As the carbon residues of the acetone and phenanthraquinone molecules do not part company during this reaction, it is highly improbable that they could have been united merely through the medium of the oxygen-atoms. The chief argument, however, in favour of the constitutional formula above given is to be found in the analogy to several similar compounds to be described in the present communication. Owing to the greater ease with which these compounds can be obtained, their reactions have been more thoroughly studied. The above formula is also in keeping with the analogy to the additive compound of orthonitrobenzaldehyde with acetone—



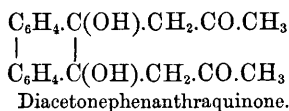
since obtained by Baeyer and Drewsen (*Ber.* **15**, 2858).

The most probable formula for acetonephenanthraquinonimide appears to be—



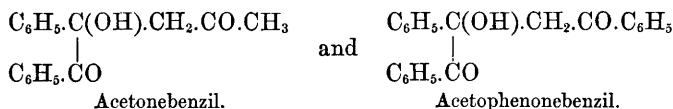
That the imido-group attaches itself to the phenanthraquinone residue, and not to the acetone residue, is rendered probable by the results which we have obtained by acting with potash solution on a mixture of phenanthraquinone and acetone. In this case no imidogen can replace the oxygen of one carbonyl-group of the phenanthraquinone: under the influence of the potash, therefore, both carbonyl-groups take part in the reaction, and an additive compound of one molecule of phenanthraquinone with *two* molecules of acetone is obtained. To this compound we assign the formula—

* This formula was first suggested by Dr. Armstrong during the discussion which followed the reading of the above-mentioned paper, but was rejected at the time by the authors of the paper.

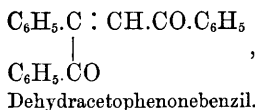


Under other conditions, we obtain an additive compound of 2 mols. of phenanthraquinone with 1 mol. of acetone. We also describe condensation compounds obtained from the above additive compounds by the elimination of the elements of water.

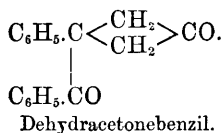
In order to extend the application of these reactions, we have studied the action of potash on mixtures of benzil with acetone and with acetophenone respectively, and have obtained the compounds—



The compound obtained from acetonebenzil by the abstraction of water has considerable theoretical interest. Whereas acetophenonebenzil parts with its hydroxyl-group along with a hydrogen-atom from the contiguous methylene-group to yield an unsaturated compound of the formula—



in the case of acetonebenzil the hydroxyl-group appears to be eliminated along with a hydrogen-atom from the methyl-group, so as to form a closed chain compound of the formula—



The evidence in favour of these views will be given in detail in the present paper.

1. PHENANTHRAQUINONE AND ACETONE.

a. *Action of a Small Quantity of Potash on a Mixture of Phenanthraquinone and Acetone.*

50 grams of very finely powdered phenanthraquinone were introduced into a small flask along with 43 grams of pure acetone* (*i.e.*, in

* Many of the reactions described in this paper yield no trace of the desired

the proportion of 1 mol. of the quinone to 3 mols. of acetone) and 2 c.c. of a strong solution of potash (sp. gr. 1.27) were then added. On shaking the flask, a reaction took place attended with considerable rise of temperature: the phenanthraquinone dissolved, and the liquid became dark-coloured. After standing over night, the whole had solidified to a yellowish-brown mass. This was broken up, then triturated with ether until completely disintegrated, poured upon a filter, and washed with ether until the liquid ran through only slightly coloured. The treatment of the filtrate will be described later on. The crude substance was thus obtained as a yellowish powder.

The first ethereal washings from the above process were almost black, and, as it seemed therefore that the strong potash had exercised a prejudicial influence, experiments were made to ascertain whether, by employing a more dilute solution of potash, a purer product could not be obtained. It was found that, under these conditions, far less heat was evolved, the solution retained its pale colour, and the quinone, without dissolving, was transformed into an almost white powder. These favourable appearances were, however, entirely deceptive. The white powder, on treatment with solvents, proved to be merely phenanthraquinone superficially coated with the new compound. In order that a complete transformation of the quinone may take place, there must be complete solution, and this, as far as our experiments go, is best effected as above by the use of strong potash, and at the expense of a portion of the material.

The yellowish powder was dissolved in boiling acetone, in which it is sparingly soluble. From the acetone solution, it was deposited, by spontaneous evaporation,* in well-formed short oblique prisms, which, after recrystallising two or three times, were quite colourless.

The new substance is sparingly soluble in the ordinary organic solvents. Glacial acetic acid and amyl alcohol dissolve it most readily, but by boiling with these solvents it is speedily decomposed. Acetone and benzene were found to be the most suitable solvents.

products unless pure acetone is employed, and for this purpose a purification by means of the bisulphite compound is necessary. In the case of one of these reactions, which with acetone from the bisulphite compound gave excellent results, we attempted to employ a sample of acetone which had been repeatedly fractionated with a Le Bel-Henninger apparatus, and showed a constant boiling point; but hardly any of the compound was obtained. We may remark that various bought specimens of acetone, ostensibly prepared "from the bisulphite compound," utterly failed to stand the test of these reactions, and yielded only resinous products from which nothing definite could be extracted.

* In a short preliminary notice of this reaction, forwarded to Berlin in English, and published in the *Berichte* (16, 282), the words of the English manuscript "by spontaneous evaporation" were transformed by the Berlin translator into "unter freiwilliger Erwärmung" ("with spontaneous rise of temperature").

The melting point cannot safely be employed as a criterion of purity. When heated, the compound turns yellow between 150° and 160°, and melts at 187°, at the same time giving off acetone. The substance which remains behind is impure phenanthraquinone.

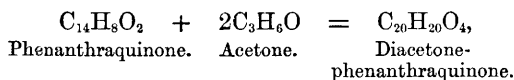
Analysis gave numbers agreeing with the formula $C_{20}H_{20}O_4$:—

	Substance.	CO ₂ .	OH ₂ .
I	0·1594	0·4321	0·0930
II	0·1550	0·4212	0·0908
III	0·1713	0·4637	0·0978

	Calculated for $C_{20}H_{20}O_4$.		Found.		
			I.	II.	III.
C ₂₀	240	74·07	73·93	74·11	73·82
H ₂₀	20	6·18	6·47	6·50	6·34
O ₄	64	19·75	—	—	—
	324	100·00			

Analyses I and II were made with one preparation; in III a second preparation was employed.

The compound has been formed according to the equation—



and we assign to it the constitution expressed by the formula already given on p. 13. In accordance with the system of nomenclature adopted by us for these compounds, it would receive the name *diacetonephenanthraquinone*.

Action of Acetic Anhydride on Diacetonephenanthraquinone.—A few grams of the compound were boiled with acetic anhydride. No more anhydride than is sufficient for solution ought to be employed, and the boiling should be discontinued as soon as everything has dissolved, otherwise only a red resin is obtained. On cooling the liquid—an operation which ought to be performed rapidly—white crystals were deposited; these were washed with ether and recrystallised from boiling benzene. The new substance was thus obtained in colourless pointed prisms, melting at 179—181°.

A further quantity of less pure substance can be separated from the acetic anhydride mother-liquor by shaking it with water; but if alcohol is employed to destroy the excess of anhydride, nothing but the red resin is obtained.

The colourless compound gave the following results on analysis :—

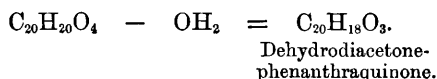
	Substance.	CO ₂ .	OH ₂ .
I.....	0·1478	0·4232	0·0840
II.....	0·1174	0·3365	0·0628

These numbers lead to the formula C₂₀H₁₈O₃ :—

	Calculated for C ₂₀ H ₁₈ O ₃ .		Found.	
			I.	II.
C ₂₀	240	78·43	78·13	78·18
H ₁₈	18	5·88	6·31	5·94
O ₃	48	15·69	—	—
	306	100·00		

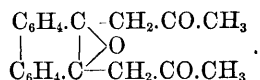
Different preparations were used in these analyses.

The compound is therefore formed from diacetonephenanthraquinone by the elimination of a molecule of water, and may be named *dehydrodiacetonephenanthraquinone* :—



There are various ways in which a molecule of water might be removed from a compound of the constitution of diacetonephenanthraquinone: our experiments do not enable us to decide between these. We could not succeed in preparing an additive compound with bromine.

Taking into consideration the fact that monacetonephenanthraquinone does not part with water when treated with acetic anhydride, it seems the most probable view that in the foregoing case the dehydration takes place between two hydroxyl-groups. Regarding diacetonephenanthraquinone as a glycol, the compound obtained by dehydration would thus be an analogue of ethylenic oxide :—



Formation of Monacetonephenanthraquinone.—The dark-coloured ethereal washings obtained in the preparation of diacetonephenanthraquinone were decolorised by shaking with freshly ignited animal charcoal. On spontaneous evaporation, the solution deposited colourless crystals of monacetonephenanthraquinone, recognisable by its melting point (90°), and its characteristic crystalline form.

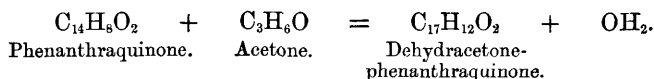
b. *Action of an Excess of Potash on a Mixture of Phenanthraquinone and Acetone.*

If an excess of the potash solution (sp. gr. 1·27) is employed in this reaction, the yield of diacetonephenanthraquinone is not so good, and the ethereal washings contain a new substance. The quantity of the latter was small; but sufficient was obtained for analysis. It was crystallised several times from boiling benzene until a constant melting point was obtained. It is deposited from the benzene solution in groups of small colourless needles, which under the microscope appear as long pointed prisms. It is moderately soluble in hot benzene or alcohol; almost insoluble in these liquids in the cold. Ether dissolves it rather readily. It melts at 195° without evolving gas.

Analysis gave figures leading to the formula $C_{17}H_{12}O_2$:—

	Substance.	CO ₂ .	OH ₂ .
I	0·1310	0·3946	0·0591
	Calculated for $C_{17}H_{12}O_2$.		Found.
C ₁₇	204	82·25	82·15
H ₁₂	12	4·85	5·01
O ₂	32	12·90	—
	248	100·00	

The compound is a condensation-product of phenanthraquinone and acetone, and we therefore propose to name it *dehydracetonephenanthraquinone* :—



It is probably formed from monacetonephenanthraquinone by elimination of a molecule of water. The corresponding transformation in the case of monacetonebenzil is described later on.

The difficulty of obtaining this substance in any quantity precluded a study of its reactions. Its constitution, however, is probably analogous to that of the corresponding condensation-product of benzil and acetone (*q.v.*).

c. *Acetonephenanthraquinone.*

In order to study the reactions of this compound, a quantity of it was prepared from acetonephenanthraquinonimide by a method mentioned by Japp and Streatfield (*Trans.*, 1882, 273), but not

further worked out by them. This method consists in the decomposition of the latter compound with an aqueous solution of oxalic acid. The following mode of applying the reaction was found to give satisfactory results: 50 grams of phenanthraquinone were shaken in a flask with 60 grams of acetone and 40 c.c. of strong aqueous ammonia, and the acetonephenanthraquinonimide thus formed was filtered off and washed with ether as described in the above-mentioned paper. Without getting rid of the adhering ether, the crude compound was suspended in water, and the resulting thick cream poured, with constant stirring, into a solution of 90 grams of crystallised oxalic acid in 800 grams of water (temperature about 25°). Almost everything dissolved; but in a short time the liquid became turbid, and the separation of minute needles of acetonephenanthraquinone commenced. After standing for two days, the compound was separated by filtration, and thoroughly washed with cold water in order to remove any oxalic acid. It was then dried by exposure to the air, and dissolved in ether. By spontaneous evaporation of the ethereal solution, the compound was obtained in large lustrous prismatic crystals. The last ethereal mother-liquors, which are rather dark, may be decolourised by shaking with freshly ignited animal charcoal. From 50 grams of phenanthraquinone, 37 grams of a pure product were obtained.

Action of Nascent Hydrogen on Acetonephenanthraquinone.—A quantity of the above compound was dissolved in cold glacial acetic acid, and zinc-dust was added in small quantities from time to time, keeping the flask in cold water. After a few days, the whole was poured into water to precipitate the substance and dissolve zinc acetate. The substance was then collected along with the excess of zinc-dust, dried at ordinary temperatures, and extracted from the zinc-dust with ether, in which it is very soluble. The impure substance, remaining after evaporation of the ether, was crystallised from hot alcohol, which removed a quantity of very soluble red gum. It was deposited from the alcoholic solution in long slender needles, which, on recrystallisation from the same solvent, melted constantly at 121°. The compound is soluble in almost all proportions in ether and chloroform, readily soluble in boiling alcohol, almost insoluble in cold alcohol. It sublimes without decomposition in feathery crystals. The yield of substance is small.

Analysis gave the following results:—

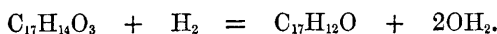
	Substance.	CO ₂ .	OH ₂ .
I.....	0.0986	0.3168	0.0488
II.....	0.1120	0.3601	0.0545

These numbers lead to the formula C₁₇H₁₂O.

	Calculated for $C_{17}H_{12}O$.		Found.	
			I.	II.
C_{17}	204	87·93	87·62	87·68
H_{12}	12	5·17	5·49	5·40
O	16	6·90	—	—
	232	100·00		

These analyses were made with different preparations of substance.

In the formation of this compound, 1 mol. of acetonephenanthraquinone takes up 1 mol. of hydrogen and parts with 2 mols. of water:—



When bromine is added to a solution of the substance in chloroform, the colour of the bromine instantly disappears, and a bromine-derivative—probably additive—separates in slender needles. The quantity obtained was not sufficient for analysis, and the preparation of a larger quantity would have involved the sacrifice of more phenanthraquinone than we could conveniently spare.

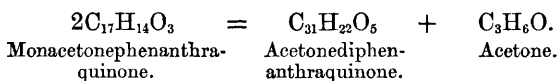
Action of Dilute Potash on Monacetonephenanthraquinone in Alcoholic Solution.—A few drops of dilute aqueous potash were added to a cold alcoholic solution of monacetonephenanthraquinone. The liquid at once assumed a yellow colour, and minute crystals adhering to the sides of the vessel soon began to form. The separation of crystals was complete in about 24 hours, when the liquid was poured off, and the crystals, which were yellow, were washed with alcohol, dried, and recrystallised from boiling benzene until they were colourless. Thus obtained, the substance forms minute rhomboidal crystals which, when heated, turn yellow at 150–160°, and melt at 190°, evolving gas and leaving an orange-coloured residue of phenanthraquinone. It is very sparingly soluble in all the usual solvents, and is deposited from its benzene solution only after long standing.

Analysis gave figures agreeing with the formula $C_{31}H_{22}O_5$:—

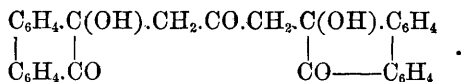
	Substance.	CO_2 .	OH_2 .
I.	0·1344	0·3858	0·0617
II.	0·1054	0·3020	0·0456

	Calculated for $C_{31}H_{22}O_5$.		Found.	
			I.	II.
C_{31}	372	78·48	78·28	78·14
H_{22}	22	4·63	4·80	4·80
O_5	80	16·89	—	—
	474	100·00		

The formation of this compound may be expressed thus :—



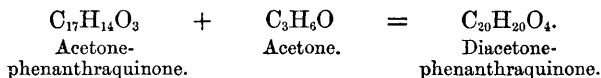
It thus contains the elements of 1 mol. of acetone with 2 mols. of phenanthraquinone, and may receive the name *acetonediphenanthraquinone*. Judging from analogy, it most probably possesses the constitution—



There are thus three distinct compounds containing the elements of phenanthraquinone and acetone in different proportions :—

Acetone.		Phenanthraquinone.		Resulting compound.
1 mol.	+	1 mol.	=	$\text{C}_{17}\text{H}_{14}\text{O}_3$ (Acetonephenanthraquinone).
2 „	+	1 „	=	$\text{C}_{20}\text{H}_{20}\text{O}_4$ (Diacetonephenanthraquinone).
1 „	+	2 „	=	$\text{C}_{31}\text{H}_{22}\text{O}_5$ (Acetonediphenanthraquinone).

Action of Strong Potash on a Solution of Acetonephenanthraquinone in Acetone.—On adding an excess of strong potash (sp. gr. 1·27) to a cold concentrated solution of acetonephenanthraquinone in acetone, the liquid became dark, and considerable heat was liberated. On cooling, the liquid layer floating on the surface of the potash solidified, and on washing the substance with ether and recrystallising it from acetone, the characteristic crystals of diacetonephenanthraquinone were obtained, melting at 187°. The following reaction had therefore occurred :—



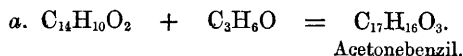
Action of Amines on Acetonephenanthraquinone.—It had already been shown (*loc. cit.*) that by the action of ammonia on acetonephenanthraquinone, one oxygen-atom of this compound could be replaced by imidogen. We, therefore, determined to study the action of amines. The reaction was allowed to take place in the cold in ethereal solution. With *ethylamine*, nothing but a green gummy mass was obtained which turned blue when treated with hydrochloric acid. With *diethylamine*, crystals were gradually deposited from the

ethereal solution. These proved to be acetonediphenanthraquinone ; so that the action of diethylamine was identical with that of potash. With *aniline*, the substance yielded nothing but a green, gummy mass.

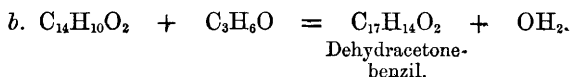
2. BENZIL AND ACETONE.

By the action of an aqueous solution of potash on a mixture of benzil and acetone, three distinct products may be obtained according to the conditions of the experiment.

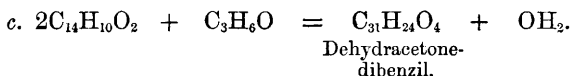
a. By acting with a small quantity of potash on benzil dissolved in an excess of acetone, the additive compound *acetonebenzil* is formed :—



b. By employing an excess of potash under conditions otherwise the same as the foregoing, a condensation-product of 1 mol. of benzil with 1 mol. of acetone is obtained :—



c. By acting with a small quantity of potash on acetone mixed with an excess of benzil, a condensation-product of 2 mols. of benzil with 1 mol. of acetone is formed :—



a. Action of a small Quantity of Potash on a Mixture of Benzil with Excess of Acetone.

50 grams of finely powdered benzil are introduced into a flask along with 30 grams of acetone,* and $\frac{1}{4}$ c.c. of strong potash (sp. gr. 1.27) is added. The flask is then corked, after which the whole is shaken until the benzil has entirely dissolved, about an hour being required for this operation. The liquid at the same time assumes a reddish colour. If, after standing for two or three days there is no sign of crystallisation, a drop of the liquid should be removed, allowed to solidify by exposure to the air, and the crystalline substance thus obtained added to the contents of the flask. The whole is again allowed to stand as long as the separation of crystals con-

* The employment of an acetone purified by means of the bisulphite compound is in this reaction *indispensable*—not merely for obtaining a good yield of the compound, but in order to obtain any of the compound at all (see note, p. 13).

tinues, a process which is generally complete in about a week. Before pouring off the still liquid portion from the crystals, it is advantageous, especially in warm weather, to allow the flask to remain for some time in a refrigerator. On the other hand, the aid of the refrigerator must not be called in before the reaction is complete, otherwise a separation of unaltered benzil will occur. The crystals, after draining from the mother-liquor, should be washed with a small quantity of ether (which must be free from alcohol, since alcoholic potash has a specific action on the substance), then dissolved in ether, and the solution allowed to evaporate spontaneously. In this way the new compound is obtained in large colourless square prisms, frequently a quarter of an inch in thickness, with flattened ends and corners generally cut off. It is deposited from a hot alcoholic solution, on cooling, in small lustrous crystals. It is readily soluble in ether and in hot alcohol; but only moderately in cold alcohol. It melts at 78° . The powdered substance, after drying over sulphuric acid, is electric.

A further quantity of the substance can be obtained from the oily mother-liquors, but it was found more advantageous to treat these with an excess of strong potash, and in this way to obtain the condensation-compound dehydracetonebenzil, $C_{17}H_{14}O_2$ (*vide infra*), which, from its sparing solubility, can more readily be purified.

Analysis of the substance gave figures leading to the formula $C_{17}H_{16}O_3$:—

	Substance.		CO ₂ .	OH ₂ .
I.	0.1190		0.3306	0.0644
II.	0.1305		0.3634	0.0718
	Calculated for		Found.	
	$C_{17}H_{16}O_3$.			
	<div style="text-align: center;">┌───────────┐</div>		<div style="text-align: center;">┌───┐</div>	
	<div style="text-align: center;">I. II.</div>		<div style="text-align: center;">I. II.</div>	
C ₁₇	204	76.11	75.76	75.91
H ₁₆	16	5.97	6.01	6.11
O ₃	48	17.92	—	—
	<hr/>	<hr/>		
	268	100.00		

The substance is therefore an additive compound of benzil and acetone in equal molecular proportion (see Equation *a*, p. 21). It would receive the name *acetonebenzil*. (For the constitutional formula of this compound see p. 17.)

Dilute potash cannot be employed with advantage in the preparation of this compound. The reaction requires a longer time than with concentrated potash, and there is the additional drawback that a larger quantity of uncrystallisable oily substance is formed.

Action of Heat on Acetonebenzil.—A weighed quantity of substance

was introduced into a tubulated flask, which was connected with another similar flask, the latter to act as receiver. The flask with the substance was heated in a sulphuric acid bath, and the receiver was cooled with ice. A little below 200° , a few drops of liquid distilled over, and at 200° the liquefied substance in the flask boiled slowly, whilst a colourless liquid collected in the receiver. The heating was continued until nothing further distilled over. The dark-coloured residue, which solidified on cooling, was weighed; and the distillate was also weighed.

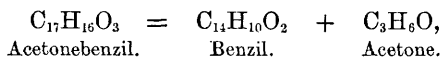
The residue was dissolved in hot alcohol. The solution, on cooling, deposited characteristic, yellow, needle-shaped crystals of benzil, melting at 94° .

The distillate had the odour of acetone, and on redistillation it boiled between 56° and 58° . Mixed with hydrogen sodium sulphite, it became hot, and, on cooling, the liquid deposited crystals of the acetone double compound.

The following are the quantitative results:—

Weight of substance	6.38 grams.
„ residue (benzil)	5.25 „
„ distillate (acetone)	1.10 „
Loss	0.03 „

Supposing the decomposition to have taken place according to the equation—



the weight of benzil obtained from the above weight of substance ought to have been 5 grams, and that of the acetone 1.38 grams. For an experiment of this kind, the above may be regarded as a sufficiently close approximation.

The decomposition is therefore analogous to that which acetone-phenanthraquinone undergoes under the influence of heat (Trans., 1882, 274).

Oxidation of Acetonebenzil.—The study of the oxidation of this compound was undertaken, less with a view of throwing light on its constitution than of comparing its behaviour towards oxidising agents with that of the condensation-product dehydracetonebenzil (*q.v.*).

By oxidation with a mixture of potassium dichromate and dilute sulphuric acid, the products obtained were benzoic and acetic acids. The formation of acetic acid is of importance in connection with the fact that the condensation-product yields no trace of acetic acid on oxidation.

We also attempted, by oxidising with chromic anhydride in acetic

acid solution, to obtain some intermediate product, but without success.

Action of Ammonia on Acetonebenzil.—20 grams of the compound were dissolved in ether, and the solution was saturated with dry ammonia. A separation of crystals commenced during the process, and, on standing, the quantity of crystalline substance increased. The liquid was poured off, the crystals washed with ether, and recrystallised from boiling alcohol, from which the compound was deposited in groups of small, colourless plates, melting at 176°. In melting, it turns red and evolves gas. The crystals also assume a faint pink colour by long exposure to the air. With hydrochloric acid and with oxalic acid, they yield a red gum.

Analysis gave results agreeing with the formula $C_{17}H_{17}NO_2$:—

	Substance.	CO ₂ .	OH ₂ .
I.	0.1316	0.3662	0.0784
II.	0.1468	0.4096	0.0880
III.	0.1228	0.3438	0.0730

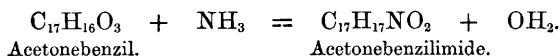
IV. 0.1104 gram burnt with cupric oxide in a vacuum gave 5.40 c.c. moist nitrogen at 14°, and under 756 mm. pressure.

V. 0.0886 gram gave 4.00 c.c. moist nitrogen at 14°, and under 759 mm. pressure.

	Calculated for $C_{17}H_{17}NO_2$.		Found.				
	I.	II.	I.	II.	III.	IV.	V.
C ₁₇	204	76.40	75.89	76.09	76.35	—	—
H ₁₇	17	6.37	6.61	6.66	6.60	—	—
N . . .	14	5.24	—	—	—	5.72	5.30
O ₂	32	11.99	—	—	—	—	—
	267	100.00					

Different preparations were employed in these analyses.

The following equation expresses the formation of this compound :—



This formation of *acetonebenzilimide*, as we propose to name the compound, corresponds with that of acetonephenanthraquinonimide (Trans., 1882, 274), from acetonephenanthraquinone and ammonia.

Action of Hydroxylamine on Acetonebenzil.—An attempt to prepare a hydroxylamine-derivative by heating the compound in alcoholic solution with hydroxylamine hydrochloride failed. The solution instantly became red on warming, and nothing but red resin was obtained. As

this was probably due to the action of the hydrochloric acid liberated in the reaction, the experiment was repeated, employing free hydroxylamine. For this purpose a quantity of acetonebenzil was dissolved in alcohol, and to this liquid a concentrated aqueous solution of two molecular proportions of hydroxylamine hydrochloride mixed with a slight excess of sodic carbonate, was added. After standing for two days, a considerable quantity of a white crystalline substance had separated. An excess of water was added in order to precipitate the organic substance and dissolve the inorganic salts. By recrystallisation from boiling alcohol, the new compound was obtained in small colourless crystals, melting at 146° . It is also moderately soluble in boiling benzene, but only sparingly soluble in ether. Hydrochloric acid converts it into a red resin.

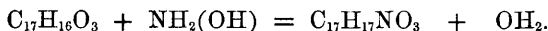
Analysis gave figures agreeing with the formula $C_{17}H_{17}NO_3$:—

	Substance.	CO ₂ .	OH ₂ .
I.	0.1371	0.3612	0.0756
II.	0.1114	0.2930	0.0616

III. 0.1070 gram burnt with cupric oxide in a vacuum gave 4.7 c.c. moist nitrogen at 17.7° , and under 763.5 mm. pressure.

	Calculated for $C_{17}H_{17}NO_3$.		Found.		
	I.	II.	I.	II.	III.
C ₁₇	204	72.08	71.85	71.73	—
H ₁₇	17	6.01	6.12	6.14	—
N	14	4.95	—	—	5.10
O ₃	48	16.96	—	—	—
	<hr/>	<hr/>			
	283	100.00			

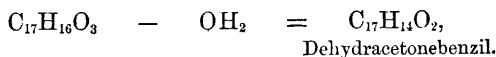
Only one molecule of hydroxylamine has therefore taken part in the condensation, and the formation of the compound is expressed by the equation—



All attempts to induce the compound thus obtained to react with a second molecule of hydroxylamine failed, although acetonebenzil must be assumed to contain two carbonyl-groups. This negative result is, however, in harmony with the investigations, since published, of Ceresole (*Ber.*, **17**, 812), who shows that di-carbonyl compounds do not react with *two* molecules of hydroxylamine, unless the carbonyl-groups are directly united.

Action of Potash on a Solution of Acetonebenzil in Acetone.—A small quantity of the compound was dissolved in acetone, and an excess of strong potash (sp. gr. 1.27) added. After standing for a day, the

solution, which had become very dark, was poured into water. The substance which separated was dried and then recrystallised from boiling benzene. It was thus obtained in yellow crystals, melting at 147° , and proved to be dehydracetonebenzil, a condensation-product of benzil with acetone described later on. The reaction had therefore taken place according to the equation—



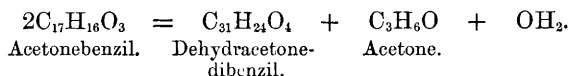
and no diacetone compound had been formed as in the case of the corresponding phenanthraquinone reaction.

Action of Dilute Alcoholic Potash on Acetonebenzil.—From 4 to 5 grams of the compound were dissolved in sufficient alcohol to keep the substance in solution in the cold, 5 drops of concentrated alcoholic potash were added, and the whole was allowed to stand in a corked flask. The solution assumed a light-red colour, and colourless lustrous crystals were gradually deposited on the sides of the flask. These were washed with alcohol and then recrystallised from benzene until the constant melting point $194\text{--}195^{\circ}$ was obtained.

Analysis led to the formula $\text{C}_{31}\text{H}_{24}\text{O}_4$:—

Substance.	CO_2 .		OH_2 .
0.1462	0.4322		0.0692
	Calculated for $\text{C}_{31}\text{H}_{24}\text{O}_4$.		
	<div style="text-align: center;">┌───────────┐</div>		
C_{31}	372	80.87	Found. 80.62
H_{24}	24	5.21	5.19
O_4	64	13.92	—
	<div style="text-align: center;">└───────────┘</div>		
	460	100.00	

The compound is identical with one described later on (dehydracetone-dibenzil) obtained by the action of potash on a mixture of acetone with excess of benzil (see also Equation c, p. 21). The reaction in which it is formed in the present case differs from the reaction of alcoholic potash with acetonephenanthraquinone (p. 20), inasmuch as with the quinone compound there was elimination of acetone only, whereas in the present case both acetone and water are eliminated:—



The action of various other reagents—phosphoric chloride, acetic anhydride, nascent hydrogen—was tried, but without yielding any definite result.

b. *Action of an Excess of strong Potash on a Mixture of Benzil with an Excess of Acetone.*

100 grams of pure acetone, 150 grams of finely powdered benzil, and 1 c.c. of potash solution (sp. gr. 1.27) were introduced into a flask, and shaken until all the benzil had dissolved; after which 20—30 c.c. of the potash solution were added, and the whole, after thoroughly shaking, was allowed to stand for a day. At the end of this time, the layer of acetone and benzil floating on the surface of the excess of potash had solidified. The potash was poured off, and the contents of the flask were shaken with hot water, which melted the crude product and removed the remains of the potash. The product, which solidified on cooling, was ground in a mortar, extracted in a flask with a small quantity of ether, and then washed on a filter with ether until the filtrate passed through only slightly coloured. In this way, the dark-coloured impurities were for the most part removed. The yellowish-grey powder thus obtained was crystallised from hot alcohol or benzene until the constant melting point 147° was obtained. The alcoholic solution deposits the compound in large, canary-yellow* prisms; from benzene it separates in tufts of needles of the same colour.

Animal charcoal had no effect in removing this colour, nor could the above melting point be altered by recrystallisation. The appearance of the compound was perfectly homogeneous, and we had no reason to suspect the presence of an impurity, especially as analysis gave figures agreeing well with those required for a condensation-product of 1 mol. benzil with 1 mol. of acetone, formed with elimination of 1 mol. of water. In an experiment, however, to be described later, in which the substance was oxidised with chromic anhydride in acetic acid solution, there was obtained, along with a new acid, a *colourless* neutral substance, which was deposited from benzene in forms indistinguishable from those of the above yellow compound, but melting at 149° . On analysis this colourless compound gave figures agreeing with the formula deduced for the yellow compound. The oxidation had therefore removed from the supposed yellow compound a coloured impurity, and had at the same time slightly raised the melting point. In order to dispel any doubt as to the identity of the white and yellow compounds, a mixture of the two was dissolved in benzene. Crystals of a *paler* yellow colour were deposited, not a mixture of white and yellow crystals.

The following are the analytical results, which lead to the formula $C_{17}H_{14}O_2$:—

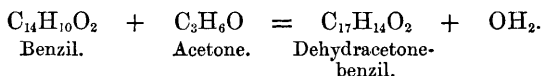
* See, however, following paragraph.

	Substance.	CO ₂ .	OH ₂ .
I	0.1176	0.3502	0.0614
II	0.1234	0.3679	0.0638
III	0.1330	0.3978	0.0686
IV	0.1348	0.4034	0.0700

	Calculated for C ₁₇ H ₁₄ O ₂ .		Found.			
			I.	II.	III.	IV.
C ₁₇	204	81.60	81.21	81.31	81.57	81.61
H ₁₄	14	5.60	5.80	5.74	5.74	5.77
O ₂	32	12.80	—	—	—	—
	250	100.00				

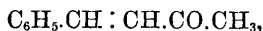
Analyses I and II were made with the yellow substance; III and IV with the colourless substance.

The formation of the compound is expressed by the equation—

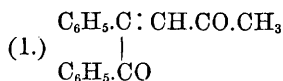


In all probability acetonebenzil is formed as an intermediate product. The conversion of acetonebenzil into this compound has been already described (p. 25). As the new compound is derived from acetonebenzil by the removal of a molecule of water, we propose to name it *dehydracetonebenzil*. It is worthy of note that this conversion cannot be effected by means of acetic anhydride.

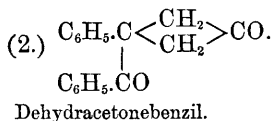
As regards the constitution of dehydracetonebenzil, *apparently* the most natural supposition would be to regard it as an analogue of Claisen and Ponder's benzalacetone,



(*Annalen*, **223**, 138), obtained by the condensation of benzaldehyde with acetone under the influence of dilute caustic soda. According to this view, it would be a benzoyl-derivative of benzalacetone and would possess the formula—



The behaviour of this compound with bromine and with oxidising agents is, however, quite incompatible with this view. Its behaviour with oxidising agents can best be accounted for by the supposition that it is a closed-chain compound of the formula—



(See also p. 13.)

*Action of Bromine on Dehydracetonebenzil.**—10 grams of the compound were dissolved in sufficient chloroform to keep the whole in solution in the cold, and a solution of bromine in chloroform was gradually added. The colour of the bromine did not disappear. After standing for some time, fumes of hydrobromic acid were given off, and a crystalline substance was deposited. Both the chloroform and the bromine had been carefully dried before using.

The crystalline substance was washed with chloroform and recrystallised from hot glacial acetic acid, from which it was deposited on cooling in slender colourless needles, melting at 172° with blackening and decomposition. It is only sparingly soluble in alcohol.

Two bromine determinations (method of Carius) gave figures pointing to a monobromo-substitution compound:—

	Substance.	AgBr.
I	0·2872	0·1627
II	0·2538	0·1458

	Calculated for $\text{C}_{17}\text{H}_{13}\text{BrO}_2$.	Found.	
		I.	II.
Br in 100 parts	24·21	24·10	24·44

In order to make perfectly sure that this monobrominated compound had not been obtained from a dibromide by decomposition during recrystallisation, a fresh quantity of the substance was prepared, washed thoroughly with cold chloroform, dried at ordinary temperatures, and then analysed. This preparation gave 26·2 per cent. of bromine, showing it to be merely an impure monobromo-compound.

A compound of formula (1) ought, judging from the analogy of benzalacetone and the other compounds prepared by Claisen, to yield a dibromide. That dehydracetonebenzil has not this formula is rendered still more probable by the fact that dehydracetophenonebenzil (*q.v.*), in which the substitution of phenyl for methyl appears to have prevented the formation of a closed chain, and which has a constitution corresponding with formula (1), readily forms an additive compound with bromine.

* For all reactions here described, the yellow compound was employed.

Oxidation of Dehydracetonebenzil.—20 grams of the yellow compound were dissolved in glacial acetic acid, and an equal weight of chromic acid—also dissolved in acetic acid—was gradually added. The mixture, which became slightly warm, was finally boiled with a reflux condenser in order to finish the reaction. It was then poured into water, which occasioned a separation of organic substance. The whole was extracted with ether, and the ethereal solution was shaken with a solution of sodium carbonate in order to remove acids. On evaporating the ether, some unattacked dehydracetonebenzil was obtained, but in a *colourless* condition.

The sodium carbonate solution was acidified with hydrochloric acid and extracted with ether. On distilling off the ether, an acetic acid solution of a new organic acid remained behind, and, by allowing the acetic acid to evaporate in a desiccator over lime, the new acid was obtained in almost colourless crystals, whilst any benzoic acid that had been formed remained in the mother-liquor. The acid was recrystallised from boiling benzene until it showed a constant melting point. Thus purified, it forms tufts of colourless needles, melting at 152° . It is readily soluble in boiling benzene, but separates almost entirely on cooling. Boiling water dissolves it sparingly.

Analysis gave the following results:—

	Substance.	CO ₂ .	OH ₂ .
I.....	0.1331	0.3682	0.0672
II.....	0.1276	0.3530	0.0642

These numbers lead to the formula $C_{16}H_{14}O_3$:—

	Calculated for $C_{16}H_{14}O_3$.		Found.	
			I.	II.
C ₁₆	192	75.59	75.44	75.44
H ₁₄	14	5.51	5.61	5.59
O ₃	48	18.90	—	—
	<hr/>	<hr/>		
	254	100.00		

A *silver salt* was prepared by precipitating a solution of the ammonium salt with silver nitrate. It forms a white powder. The dry salt is electric. It gave the following figures on combustion:—

Substance.	CO ₂ .	OH ₂ .	Ag.
0.1418	0.2752	0.0466	0.0424

	Calculated for $C_{16}H_{13}O_3Ag$.		Found.
C_{16}	192	53.18	52.92
H_{13}	13	3.60	3.64
Ag	108	29.92	29.90
O_3	48	13.30	—
	361	100.00	

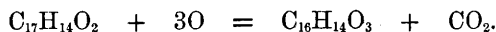
The *barium salt* was obtained by boiling the acid with *barium carbonate*, and allowing the solution to evaporate over sulphuric acid. Like all the soluble salts of this acid which we examined, its difference of solubility in hot and cold solutions is very slight. It was obtained in rosettes of flat prisms of the formula $(C_{16}H_{13}O_3)_2Ba, 2OH_2$. It parts with its water of crystallisation at 100° .

0.3064 gram of air-dried salt lost at 100° 0.0160 gram, and the resulting 0.2904 gram anhydrous salt gave 0.1042 gram barium sulphate.

	Calculated for $(C_{16}H_{13}O_3)_2Ba, 2OH_2$.	Found.
OH_2 in 100 parts	5.30	5.22

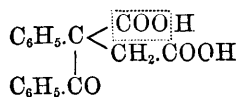
	Calculated for $(C_{16}H_{13}O_3)_2Ba$.	Found.
Ba in 100 parts	21.30	21.09

The acid is formed from dehydracetonebenzil according to the equation—

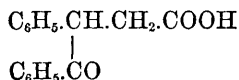


Supposing dehydracetonebenzil to possess the constitution represented by formula (1), the oxidation of such a compound to an acid of the formula $C_{16}H_{14}O_3$ would be very difficult to account for. It would be necessary to assume that the methyl-group at the end of the chain is oxidised away, the carbonyl-group converted into carboxyl, and that then the two unsaturated carbon-atoms, under conditions which generally lead to the separation of such atoms, take up, in presence of a powerful oxidising agent, hydrogen and become saturated.

On the other hand, by adopting formula (2) for dehydracetonebenzil, the formation of the acid can be explained. In the first place by a separation of the carbonyl from one of the methylene-groups in the closed chain, and by conversion of these separated groups into carboxyl-groups, an acid of the formula



would be obtained. This acid is a bibasic ketonic acid. It is well known that ketonic acids vary greatly in stability according to the class to which they belong. Those ketonic acids are stable in which carboxyl and carbonyl are directly united, as in pyruvic acid, or in which carboxyl and carbonyl are attached to different carbon-atoms, as in lævulic (β -acetylpropionic) acid; those are unstable, in which carboxyl and carbonyl are attached to the same carbon-atom, as in the case of acetoacetic acid: such acids readily part with carbonic anhydride, yielding a ketone. An acid of the above formula would unite in itself the properties of two of the above classes; it would be unstable as regards the carboxyl-group attached to the same carbon-atom as the benzoyl-group; and it would be stable as regards the other carboxyl-group. Under the conditions of the oxidation experiment, this acid would part with carbonic anhydride from the first of these carboxyl-groups (as indicated in the formula), yielding the monobasic acid:—



which would thus be β -benzoylhydrocinnamic acid.

Although we regard the above as the most probable of the various constitutional formulæ that might be suggested for the acid, we must call attention to the fact that the only reactions which we have tried in confirmation of this constitution have yielded negative results. Thus, by the action of nascent hydrogen we hoped to obtain a lactone; but after subjecting the acid for some days to the action of sodium-amalgam, nearly the whole of the original substance was recovered unchanged, and only a trace of an indifferent oil was formed, which, however, did not appear to be a lactone, as it did not dissolve in caustic alkalis on heating.* We further hoped, by the action of hydroxylamine, to prove the ketonic character of the acid; but no action took place with hydroxylamine hydrochloride in aqueous alcoholic solution at 100°.

The various other constitutions that might be suggested for this acid—thus that it is an acid of the glycidic type, or that it is an unsaturated acid containing an alcoholic hydroxyl-group—are still less in keeping with its reactions and mode of formation.

The chief obstacle to a thorough study of this acid is the difficulty of obtaining it in any considerable quantity, the yield being very small.

As a dehydracetonebenzil of formula (1) ought to yield acetic acid on oxidation, it seemed of importance to show that this acid was not

* Of course this insolubility in caustic alkalis does not absolutely prove that the oil was not a lactone.

formed, especially as acetonebenzil readily yields acetic acid. A quantity of dehydracetonebenzil was therefore boiled with a mixture of dilute sulphuric acid and potassium dichromate, until all action had ceased. The liquid was then distilled until about a third had passed over; the distillate was filtered from benzoic acid, neutralised with sodium carbonate, and evaporated to dryness. Not the slightest trace of acetic acid could be obtained from this residue.

Another portion of dehydracetonebenzil was oxidised with a 5 per cent. permanganate solution in the cold. The filtrate from the manganese dioxide, when acidified and extracted with ether, yielded as chief product benzoic acid, along with a small quantity of benzoylformic acid, identified by means of the characteristic thiophene reaction. We satisfied ourselves that β -benzoylhydrocinnamic acid does not give this reaction.

The action of the following reagents upon dehydracetonebenzil was also tried, but without definite result:—acetic anhydride, alcoholic ammonia, potash (fusion), hydriodic acid and amorphous phosphorus, zinc-dust at higher temperatures, zinc-dust with acetic acid.

c. Action of a Small Quantity of Potash on a Mixture of Acetone with Excess of Benzil.

50 grams of finely powdered benzil were introduced into a flask with 20 grams of pure acetone and $\frac{1}{2}$ c.c. of potash solution (sp. gr. 1.27). The flask was shaken until all the benzil had dissolved, this process requiring about an hour. After standing for a day, the contents of the flask, which were almost solid, were shaken with ether. A small quantity of acetonebenzil went into solution and a sparingly soluble white crystalline powder remained, which, after washing with ether, was recrystallised from benzene until the constant melting point $194-195^\circ$ was obtained.

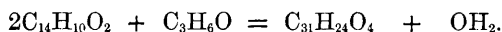
Besides acetonebenzil, the ethereal washings contained an uncrystallisable gum, which, however, by shaking with more potash, could be converted into the sparingly soluble crystalline compound.

Analysis gave results agreeing with the formula $C_{31}H_{24}O_4$:—

	Substance.	CO ₂ .	OH ₂ .
I.	0.1194	0.3520	0.0570
II.	0.1420	0.4182	0.0666
III.	0.1656	0.4874	0.0790

	Calculated for		Found.		
	$C_{31}H_{24}O_4$.		I.	II.	III.
C_{31}	372	80·87	80·40	80·32	80·27
H_{24}	24	5·21	5·30	5·21	5·30
O_4	64	13·92	—	—	—
	460	100·00			

The compound is identical with that obtained by the action of dilute alcoholic potash on acetonebenzil (p. 26). Its formation in the present case occurs by the abstraction of 1 mol. of water from 2 mols. of benzil and 1 mol. of acetone. It would therefore receive the name *dehydracetonedibenzil* :—



Dehydracetonedibenzil is almost insoluble in cold benzene and alcohol; even boiling alcohol dissolves it but sparingly. The best solvent is boiling benzene, from which it is deposited, after some time, in well-formed colourless crystals. From the alcoholic solution, it separates with 1 mol. of alcohol of crystallisation, which is retained at 100° , but given off at 120° . When the crystals containing alcohol of crystallisation are heated in a capillary tube they melt at 158 — 160° .

Alcohol of crystallisation was determined with the following result :—

0·2410 gram air-dried substance, containing alcohol of crystallisation, lost at 120° 0·0222 gram.

	Calculated for	Found.
	$C_{31}H_{24}O_4 \cdot C_2H_6O$.	
C_2H_6O in 100 parts	9·09	9·21

3. BENZIL AND ACETOPHENONE.

a. Action of Potash in the Cold on a Mixture of Benzil and Acetophenone.

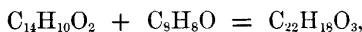
Equal molecular proportions of acetophenone and finely powdered benzil were shaken in a flask with an excess of strong potash (sp. gr. 1·27) and allowed to stand. At first the potash solution remained in suspension, but after a few days it separated, whilst the organic substance formed a solid cake on the surface. This cake was ground with water, thoroughly washed, and, after drying, shaken with ether. The greater part dissolved, leaving a yellow powder, which proved to be dehydracetophenonebenzil, a compound to be described later. On spontaneous evaporation, the ethereal solution deposited large colourless oblique prisms, and the mother-

liquor from these crystals yielded a further quantity of the same substance, contaminated however with unchanged benzil. By crystallisation from alcohol, the colourless substance was obtained pure in flat oblique prisms, melting at 102° . It is readily soluble in ether and in boiling alcohol, sparingly soluble in alcohol in the cold. When heated above its melting point, it gives off acetophenone, which may be recognised by its odour.

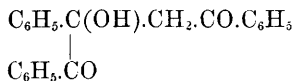
Analysis gave numbers agreeing with the formula $C_{22}H_{18}O_3$:—

	Substance.	CO ₂ .	OH ₂ .
I.	0.1426	0.4170	0.0724
II.	0.1498	0.4378	0.0756
	Calculated for $C_{22}H_{18}O_3$.		Found.
			I. II.
C ₂₂	264	80.00	79.75 79.70
H ₁₈	18	5.45	5.64 5.60
O ₃	48	14.55	— —
	<hr/>	<hr/>	
	330	100.00	

The formation of this compound is expressed by the equation—



and it would receive the name *acetophenonebenzil*. Its constitutional formula would be—



b. *Action of Potash, aided by Heat, on a Mixture of Benzil and Acetophenone.*

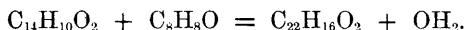
The ingredients were mixed as in the preceding experiment; but heat was applied until the whole of the benzil had fused, after which the flask was allowed to stand for some hours at a temperature sufficiently high to prevent solidification. On allowing the flask to cool, the layer of organic substance floating on the surface of the potash solidified. The solid cake was treated as in the former experiment. This time, the ethereal extract contained only a small quantity of a reddish oil and a trace of unaltered benzil. No acetophenonebenzil was formed on this occasion. The portion undissolved by the ether was recrystallised from hot alcohol, until it exhibited the constant melting point 129° . It crystallises in tufts of flat pointed yellowish needles, which are very sparingly soluble in ether and in cold alcohol, but dissolve readily in boiling alcohol.

The analytical figures agreed with the formula $C_{22}H_{16}O_2$:—

	Substance.	CO ₂ .	OH ₂ .
I.	0.1582	0.4900	0.0748
II.	0.1296	0.4010	0.0628

	Calculated for $C_{22}H_{16}O_2$.		Found.	
			I.	II.
C ₂₂	264	84.61	84.47	84.38
H ₁₆	16	5.13	5.25	5.38
O ₂	32	10.26	—	—
	312	100.00		

This compound is formed by the condensation of a molecule of benzil with a molecule of acetophenone :—



It may therefore receive the name *dehydracetophenonebenzil*.

Action of Bromine on Dehydracetophenonebenzil.—The compound was dissolved in cold chloroform, avoiding an excess of the solvent, and one molecular proportion of bromine was added. On standing, the colour due to the bromine gradually became much fainter, without however entirely disappearing, and a bromine-derivative was deposited in large crystals. There was no evolution of hydrobromic acid. The crystals were of a reddish colour, and, when exposed to the air, gave off a faint odour of bromine, even after standing for some days, at the same time becoming opaque. As it was found impossible to recrystallise this substance without decomposition, the freshly prepared crystals were washed with chloroform, exposed for a short time to the air, powdered, the powder dried for two hours over sulphuric acid, and in this condition analysed. A bromine estimation (Carius) gave figures which were somewhat too high for a *tetrabromide*—an entirely unexpected result.

0.1864 gram of substance gave 0.2278 gram of silver bromide.

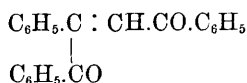
	Calculated for $C_{22}H_{16}O_2Br_4$.	Found.
Br in 100 parts.	50.63	52.00

Heated in a capillary tube the substance becomes dark at about 70°, turns pale again at about 80°, and melts between 110° and 115°.

The bromine was in a state of very unstable combination. A portion of the substance which had been allowed to remain for some weeks in a desiccator over lime, had parted with nearly the whole

of its bromine, and was found, after recrystallisation from alcohol, to have been reconverted into dehydracetophenonebenzil.

We are unable satisfactorily to explain the formation of a tetrabromide. A dehydracetophenonebenzil of the formula—



ought to yield a dibromide, and it is conceivable that this dibromide might form a molecular compound with a second molecule of bromine, similar to the molecular compounds of acetic acid with bromine and hydrobromic acid. In any case, the action is anomalous and deserves further study. For the present, however, we regard this reaction as sufficient evidence of the unsaturated character of dehydracetophenonebenzil, and the foregoing is the only probable constitutional formula which would represent it as an unsaturated compound.

The fusing points of dehydracetonebenzil and dehydracetophenonebenzil also render it probable that these compounds do not belong to one and the same category. Whereas acetophenonebenzil, a compound which may be regarded as derived from acetonebenzil by the substitution of phenyl for methyl, fuses higher than acetonebenzil, dehydracetophenonebenzil fuses 20° lower than dehydracetonebenzil. The high melting point of the latter compound is probably due to the fact that it is, as assumed in this paper, a closed-chain compound.

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