[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MCGILL UNIVERSITY]

The Reactions of Anhydracetonebenzil. II[1]

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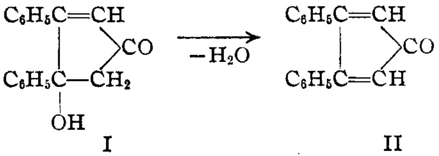
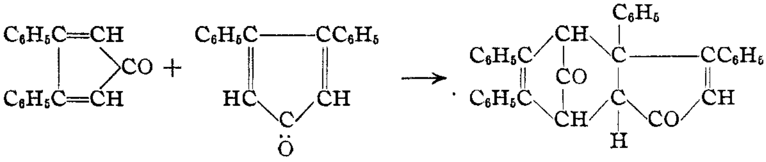
The most characteristic reaction of anhydracetonebenzil (I) is the ease with which it loses water and forms a "bimolecular product" when treated with acidic dehydrating agents. Japp[2] and Gray[3] observed that the homologs of (I) exhibited the same behavior, as long as there was one hydrogen left in the alpha position and adjacent to the hydroxyl group, but neither suggested a possible structure for the new type of substance. They also found that the latter lost quantitatively one molecule of carbon monoxide on pyrolysis, and that the resulting product formed a monophenylhydrazone. The problem has been investigated in this Laboratory and the results are described in this communication.

In a previous paper[4] it was suggested that a cyclopentadienone (II) was the primary product of dehydration, although it was never isolated.



I II

This substance contains two conjugated systems, one that of an α,β-unsaturated ketone and the other that of a diene, so should enter into a diene synthesis with itself. Assuming that it did so, it was possible to write the structure (III) for the bimolecular product; its correctness was then verified by a long series of reactions that ultimately gave *o*-diphenylbenzene.



III

This tricyclic ketone forms a dioxime; the carbonyl groups are not linked alike, one being removed readily as carbon monoxide on heating. *A priori*, it would be expected that the bridge would be more easily lost, leaving a bicyclic ketone (IV); the presence of a conjugated system in (IV) was shown by the addition of maleic anhydride to give (V)—the latter could be more conveniently prepared directly from the bimolecular product

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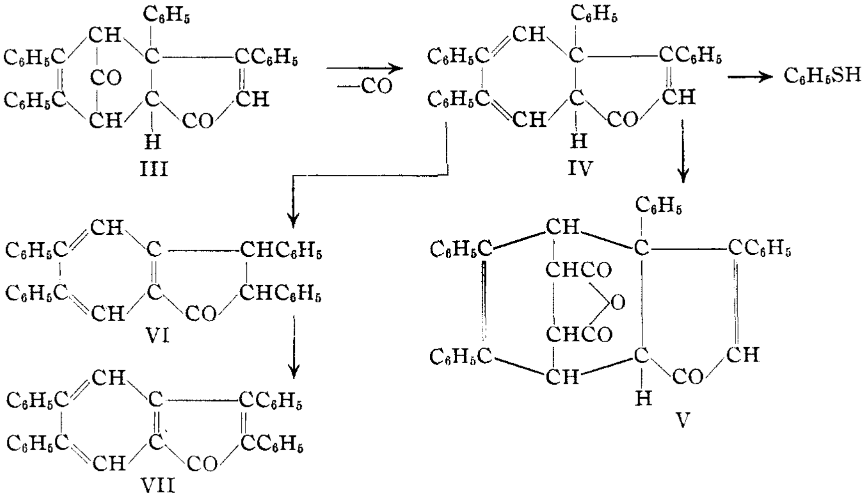
[1] This paper is a more extended presentation of results originally embodied in a Communication to the Editor received November 25, 1932.

[2] Japp and co-workers. This long list of references is given in detail in the previous paper.[4]

[3] Gray, *J. Chem. Soc.*, **95**, 2131 (1909).

[4] Allen and Spanagel, THIS JOURNAL, **54**, 4338 (1932).

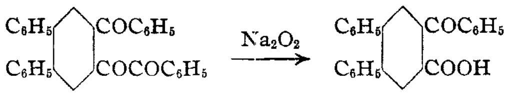
(III), because the ketone (IV) very easily underwent a rearrangement on pyrolysis, resulting in the indanone (VI).



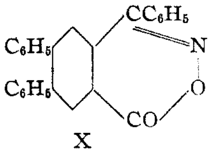
The bicyclic ketone (IV) is pale yellow, forms an oxime and yields thiophenol when heated with sulfur. The use of sulfur to detect alkyl radicals attached to carbon atoms common to two rings has been widely employed by Ruzicka[5] but this is the first instance of which we are aware when an aryl group has been so removed.

The indanone (VI) is colorless; it does not react with maleic anhydride but forms a monophenylhydrazone corresponding in physical properties with the one described by Japp, so that his pyrolysis product was probably (VI); this is to be expected since it is only by working cautiously that (IV) survives the heating necessary to remove the carbonyl bridge. It is easily dehydrogenated by sulfur to the deep red indone (VII); the color of the latter is deeper than that of diphenylindone.[6]

This red ketone forms an oxime and mono-*p*-bromophenylhydrazone, and is readily oxidized to a yellow triketone (VIII), but does not add maleic anhydride. The triketone is cleaved by sodium peroxide to benzoic acid and a ketonic acid (IX); when the preparation of an oxime of the latter was attempted, an indifferent compound containing nitrogen resulted—it was not affected by phosphorus pentachloride and had no active hydrogen, and probably is best represented as the orthoxazine (X).



VIII IX



X

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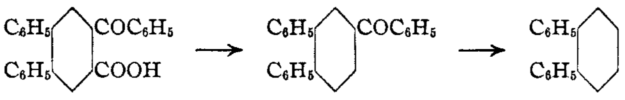
(5) Ruzicka, *Helv. Chim. Acta*, **5**, 349 (1922).

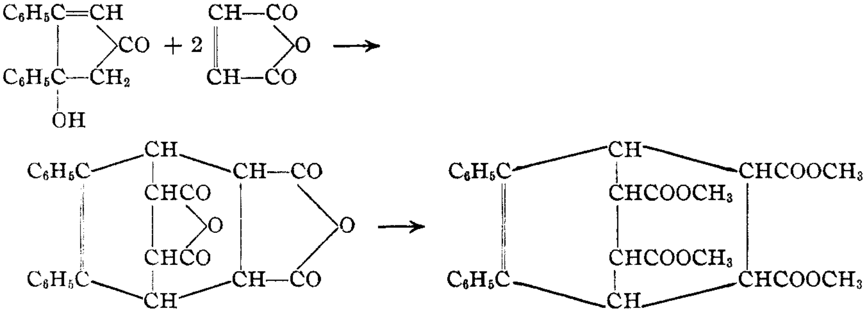
(6) Heyl and Meyer, *Ber.*, **28**, 2776 (1895).

On decarboxylation of the acid (IX) a diphenylbenzophenone was obtained in poor yield; it formed a monoxime which by the Beckmann rearrangement gave an uncrystallizable anilide. This was hydrolyzed to a glass-like amine which, when diazotized in alcoholic hydrochloric acid and warmed with copper powder, gave an oil from which *o*-diphenylbenzene was separated by vacuum distillation.



IX

The transient existence of the cyclopentadienone (II) can be shown by using an excess of maleic anhydride as a dehydrating agent for anhydracetonebenzil; on heating to about 200°, carbon monoxide and water are lost and a solid dianhydride (XI) is formed; the latter is readily converted into a tetramethyl ester. The reaction proceeds in steps, but the description of the intermediate products and their reactions, along with a similar series from tetraphenylcyclopentadienone, will form the subject of a later communication. It is sufficient here to note the similarity to Diels' reactions between coumalin and maleic anhydride.[7]



XI

After a clue had been obtained as to the structure of the bimolecular product, one analogous case was discovered in the literature; Zincke[8] prepared a highly chlorinated cyclopentenone (XII) and found that on reduction with stannous chloride a bimolecular product was obtained; when heated, the latter lost chlorine and carbon monoxide to form a perchlorindone (XIII); the carbonyl group was detected by chlorination with phosphorus pentachloride. He likewise assumed that a cyclopentadienone was the primary product and converted the indone into tetrachlorophthalic acid to show the presence of a benzene ring.

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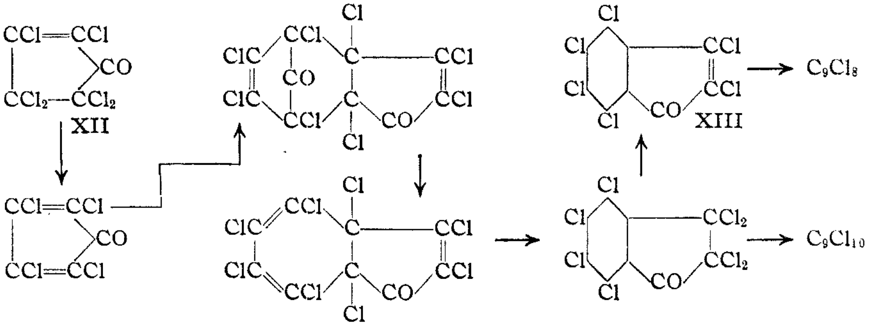
(7) Diels, Alder and Müller, *Ann.*, **490**, 257 (1931).

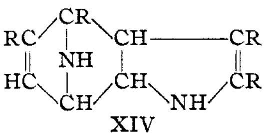
(8) Zincke and co-workers, *Ber.*, **21**, 2719 (1888); **22**, 486 (1889); **23**, 812 (1890); **26**, 2104 (1893); *Ann.*, **272**, 243 (1892); **292**, 135 (1897); **367**, 1 (1909); **394**, 7 (1912).


XII

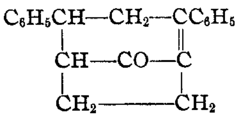
XIII

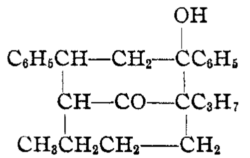
Since then the structure of dicyclopentadiene has been shown to be of a similar nature.[9]

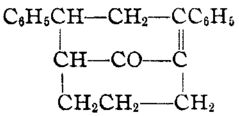
The above work suggests that the dipyrroles are similarly constituted and should be represented as in formula (XIV). The correctness of this assumption is being tested.


XIV

Very few other substances having a carbonyl bridge are known; Stobbe[10] has described two (XV, XVI) and a third (XVII) has been prepared in this Laboratory. None of them lose carbon monoxide when heated unless the molecule is entirely decomposed; from a study of mechanical models it was evident that in the latter type the CO bridge formed part of a strainless ring, whereas it was impossible to construct a model of the diketone (III) described in this paper without great distortion. A previous attempt to prepare an unsaturated bicyclic system having a carbonyl bridge was unsuccessful.[11]


XV


XVI


XVII

Experimental

A. Dehydrogenation of Anhydracetonebenzil; "the Bimolecular Compound"; 3a,4,7,7a-Tetrahydro-3,3a,5,6-tetraphenyl-4,7-methanoindene-1,8-dione (III).—An almost quantitative yield was obtained by warming a mixture of 60 g. of glacial acetic acid, 50 g. of finely powdered anhydracetonebenzil and 10 cc. of concd. sulfuric acid nearly to boiling with frequent shaking, until the deep red color had changed to a light brown (about ten minutes). The substance separated on cooling and was purified by crystallizing from a benzene–alcohol mixture. It formed two dioximes when treated with hydroxylamine acetate in the usual way. After two hours of heating one was isolated in the form of rods, readily soluble in alcohol, m. p. 176°; the isomer was the

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[9] Alder and Stein, *Ann.*, **485**, 211, 223 (1931).

[10] Stobbe, *J. prakt. Chem.*, **86**, 210 (1912).

[11] Allen, *Can. J. Res.*, **4**, 264 (1931).

principal product after twenty-four hours of heating—it is only slightly soluble in alcohol; m. p. 229°.

Anal. Calcd. for $C_{34}H_{28}O_2N_2$: N, 5.7. Found: (229°) N, 5.7; (176°) N, 5.1.

When acetic anhydride and sulfuric acid are used for the dehydration a small amount of an acetate can be isolated by careful manipulation; this is very soluble in the usual organic solvents; it separates from alcohol in clusters of prisms, m. p. 91°.

Anal. Calcd. for $C_{19}H_{16}O_3$: C, 78.1; H, 5.5. Found: C, 77.9, 77.8; H, 5.3, 5.1

On hydrolysis with dilute ammonia the bimolecular compound resulted, but alcoholic potash gave a new substance that crystallized in thick prisms, m. p. 280°.

Anal. Found: C, 85.2, 84.8; H, 5.3, 6.2.

It does not react with acetyl chloride, or acetic anhydride and sulfuric acid; owing to the small amount available it was not further investigated.

B. Pyrolysis of (III); Preparation of the Isomers, 3a,7a-Dihydro-3,3a,5,6-tetraphenylinden-1-one (IV) and 2,3,5,6-Tetraphenylindan-1-one (VI).—In a small flask 25 g. of the bimolecular product was heated by a metal bath at 210° for ten minutes; carbon monoxide was evolved rapidly. The cooled melt was dissolved in benzene and alcohol added to precipitate 10 g. of the white indanone (V); the filtrate slowly deposited 10 g. of the yellow isomer. After purification the white substance melted at 176°, and the pale yellow isomer at 167°; mixed melting points showed a marked depression. The indanone (VI) is fairly soluble in acetone, acetic acid and benzene, but only slightly soluble in alcohol and ether; it crystallizes in characteristic five-sided plates. It did not decolorize permanganate or bromine instantly. It is undoubtedly the substance described by Japp, though he gave a range of melting points.

Anal. Calcd. for $C_{33}H_{24}O$: C, 90.8; H, 5.5. Found: C, 90.9; H, 5.5.

The oxime, prepared in the usual way, separated from alcohol in leaflets, m. p. 225°.

Anal. Calcd. for $C_{33}H_{25}ON$: N, 3.1. Found: N, 3.0.

It gave a phenylhydrazone of m. p. 250° as previously described.

C. The Yellow Ketone (IV).—It was difficult to secure this substance unless the temperature of the pyrolysis was very carefully controlled; on heating too long or at a higher temperature it rearranges to the indanone—this change even takes place slowly in boiling alcoholic solutions.

It is readily soluble in acetone, benzene and decalin but sparingly in alcohol and ether; it separates in yellow rods from alcohol, m. p. 167°.

Anal. Calcd. for $C_{33}H_{24}O$: C, 90.8; H, 5.5. Found: C, 90.7; H, 5.4.

The oxime, made by the customary procedure, crystallized from alcohol in fine yellow prisms, m. p. 130° (unsharp).

Anal. Calcd. for $C_{33}H_{25}ON$: N, 3.1. Found: N, 3.5.

It gave a phenylhydrazone, m. p. 250°, probably the same as the one from the indanone, since a mixed melting point showed no depression. This may be accounted for by the ease of rearrangement noted above, which takes place during the sealed tube treatment required to prepare the phenylhydrazone.

Anal. Calcd. for $C_{39}H_{30}N_2$: N, 5.3. Found: N, 5.4.

It added maleic anhydride to form the tetracyclic substance (V), but a large part was isomerized at the same time to the indanone; the new product was more conveniently prepared from the bimolecular compound. The indanone did not react with maleic anhydride.

3a,4,5,7,7a-Hexahydro-1-keto-3,3a,8,9-tetraphenyl-4,7-ethanoindene-5,6-dicarboxylic Anhydride (V).—A mixture of 5 g. of the bimolecular compound and an equal weight of maleic anhydride was heated by an oil-bath at the boiling point as long as carbon monoxide was given off (fifteen minutes), cooled and 15 cc. of methyl alcohol added to remove the excess anhydride; the 4 g. of solid that was insoluble was recrystallized from acetic anhydride, from which it separated in rods, m. p. 301°. It is slightly soluble in alcohol, but very soluble in acetic acid, acetic anhydride and acetone.

Anal. Calcd. for $C_{37}H_{26}O_4$: C, 83.1; H, 4.9; mol. wt., 534. Found: C, 83.3; H, 5.0; mol. wt., 549.

It dissolved readily in dilute sodium hydroxide, but the acid obtained by acidification turned into the anhydride so easily that no attempt was made to obtain it pure.

On heating 10 g. of (IV) with 1 g. of flowers of sulfur in a small distilling flask at 325°, under slight suction, for a half hour it became black, but 0.2 g. of thiophenol collected in the receiver; the latter was converted into the 2,4-dinitrophenyl thioether, m. p. 121°, by Bost's procedure;[12] a mixed melting point with an authentic specimen showed no depression, m. p. 121°. Nothing could be separated from the black residue; if the temperature was kept lower, only an odor of thiophenol was noticed, and the rearrangement product (the indanone) was found—this doubtless accounted for the low yield of thiophenol; the sulfur reaction requires a higher temperature than the isomerization.

D. The Indenone (VII).—The indanone was readily dehydrogenated by heating with sulfur to give the new red ketone; the latter was oxidized with scission of the five-membered ring to a 1,2-diketone (VIII) which was readily cleaved by sodium peroxide; the keto acid (IX) thus resulting gave an indifferent substance containing nitrogen when treated with hydroxylamine acetate—presumably the orthoxazine (X).

2,3,6,7-Tetraphenylinden-1-one (VII).—A mixture of 25 g. of the pure indanone and 1 g. of flowers of sulfur in a small distilling flask under slight suction was heated for a half hour at 325°; hydrogen sulfide was evolved and the mass became a deep red. When cold, ether was added, the unused sulfur filtered, and on addition of alcohol and partial evaporation 16 g. (65%) of the red ketone crystallized. It is readily soluble in ether, acetone, acetic acid and benzene, but only slightly soluble in the alcohols; it forms red rods, m. p. 166°.

Anal. Calcd. for $C_{33}H_{22}O$: C, 91.2; H, 6.1. Found: C, 91.1; H, 5.1.

The yield was not increased by varying the temperature, amount of sulfur or addition of copper sulfide. It could be made, without isolation of the intermediates, from pure bimolecular product, if the latter was first heated to 250° for some time before the addition of the sulfur. The oxime, prepared as usual, crystallized from chloroform in fine yellow needles, m. p. 292°.

Anal. Calcd. for $C_{33}H_{23}ON$: N, 3.1. Found: N, 3.2.

The *p*-bromophenylhydrazone was never obtained pure; a brownish product was separated from the reaction mixture and repeatedly crystallized from *n*-butyl alcohol until it had a constant melting point, 226°.

Anal. Calcd. for $C_{39}H_{27}N_2Br$: Br, 13.2. Found: Br, 11.4, 11.9, 13.7.

1,2-Diphenyl-4-benzoyl-5-phenylglyoxylbenzene (VIII).—To a suspension of 10 g. of finely powdered red ketone in 60 cc. of acetic acid was added 8 g. of chromic acid, and the mixture refluxed for ten minutes; on addition of 300 cc. of ice water a fine yellow solid separated. This was filtered, dried and recrystallized from benzene and alcohol, from which it separated in yellow rosets, m. p. 183°. The yield was 7.9 g. (78%). It is slightly soluble in alcohol and ether, but readily soluble in benzene, acetone and acetic acid.

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[12] Bost, Turner and Norton, THIS JOURNAL, **54**, 1985 (1932).

Anal. Calcd. for $C_{33}H_{22}O_3$: C, 85.0; H, 4.7. Found: C, 85.1, 85.1; H, 5.0, 4.7.

The same substance was obtained in a smaller yield by the use of permanganate in acetone. The quinoxaline was prepared nearly quantitatively in the usual manner; it is sparingly soluble in alcohol, but crystallizes well from that solvent in cubes, m. p. 184°.

Anal. Calcd. for $C_{39}H_{26}ON_2$: N, 5.2; mol. wt., 538. Found: N, 5.0; mol. wt., 540.

E. 2-Benzoyl-4,5-diphenylbenzoic Acid (IX); Cleavage of the Diketone.—A solution of 5 g. of sodium peroxide in 50 cc. of ice water was added slowly with vigorous shaking to a suspension of 10 g. of the finely powdered triketone in 100 cc. of alcohol; the yellow solid slowly dissolved and shiny flakes formed. After a half hour the mixture was poured into water (filtered if necessary) and acidified with acetic acid—the acid slowly separated, was filtered after five hours, and recrystallized from dilute methyl alcohol. It is very soluble in organic solvents and dilute alkaline solutions. The yield was 7.6 g. (90%); m. p. 250°.

Anal. Calcd. for $C_{26}H_{18}O_3$: C, 82.5; H, 4.8. Found: C, 82.0; H, 4.7.

The filtrate was steam distilled and the benzoic acid identified in the usual way. When 1 g. of the keto acid was refluxed with hydroxylamine acetate in alcohol, white needles separated almost quantitatively, after an hour; the new product is almost insoluble in alcohol, but very soluble in benzene and chloroform; it slowly dissolves in dilute potash after long boiling. It melts at 225°.

Anal. Calcd. for $C_{26}H_{17}O_2N$: N, 3.7. Found: N, 3.5, 3.4.

It was recovered unchanged after an attempted Beckmann rearrangement using phosphorus pentachloride in absolute ether for twenty-four hours.

F. The Keto Acid (IX) and its Degradation to *o*-Diphenylbenzene.—The yields in each step were very low from this point on.

3,4-Diphenylbenzophenone.—A mixture of 5 g. of the keto acid and 0.5 g. of copper carbonate was heated at 225° for twenty minutes in a small distilling flask and then distilled *in vacuo;* the pale yellow oil was taken up in acetone—after dilution with methyl alcohol white prisms slowly separated; the yield was 1.5 g. (34%), m. p. 133°. It is soluble in the common organic solvents except alcohol.

Anal. Calcd. for $C_{25}H_{18}O$: C, 89.8; H, 5.4. Found: C, 89.9; H, 5.5.

The oxime crystallized from dilute alcohol in fine, white needles, m. p. 156°; the yield was 50%.

Anal. Calcd. for $C_{25}H_{19}ON$: N, 4.0. Found: N, 4.3.

A mixture of 1 g. of the oxime, 1.5 g. of phosphorus pentachloride and 20 cc. of absolute ether was left for a day at room temperature, then poured into water, the ether layer separated, dried with sodium sulfate and the solvent allowed to evaporate; 1 g. of a viscous oil remained—it could not be purified so was hydrolyzed by refluxing with alcoholic potash; on dilution with water an oil precipitated and was extracted with ether—it gave a strong qualitative test for nitrogen. Since it showed no tendency to crystallize it was taken up in 5 cc. of alcohol, 6 cc. of 1:1 hydrochloric acid added, the mixture well cooled and 0.2 g. of sodium nitrite introduced; when 0.1 g. of copper powder was dropped in gas bubbles became visible, and after a short warming ether was added, the upper layer separated, dried over sodium sulfate and distilled *in vacuo.* The 0.2 g. of pale yellow oil that was obtained slowly crystallized on standing; it had a melting point of 56° and showed no depression when mixed with some authentic *o*-diphenylbenzene.

G. The Reaction of Anhydracetonebenzil with Excess Maleic Anhydride; 7,8-Diphenylbicyclo-(2,2,2)-7-octene-2,3,5,6-tetracarboxylic Acid Dianhydride (XI).—In order to show that diphenylcyclopentadienone (II) was capable of at least a transitory existence,[13] it was heated with maleic anhydride as a dehydrating agent, and a sufficiently large excess used to allow for addition to the diene linkage. Equal weights of the two substances were heated in an oil-bath at 170°; the melt appeared to boil vigorously and carbon monoxide was evolved rapidly and burned with a large blue flame. The temperature was gradually raised until at about 230° the melt suddenly solidified; it was cooled somewhat, *p*-cymene added and the suspension filtered. The excess anhydride was washed out with hot methyl alcohol and the crude product recrystallized from *p*-cymene or acetic anhydride. It formed white flakes, shrinking at 334°, becoming liquid at 346° and giving off a gas at 356°.

Anal. Calcd. for $C_{24}H_{16}O_6$: C, 72.0; H, 4.0. Found: C, 71.5; H, 4.0.

It is insoluble in the alcohols, ether, acetone and carbon tetrachloride, sparingly soluble in *p*-cymene, but very soluble in ethyl acetate and acetic anhydride. It dissolves in sodium hydroxide; on acidification an acid is precipitated in fine needles—the melting point is indefinite as it loses water and re-forms the anhydride.

The tetramethyl ester was prepared by saturating a mixture of 5 g. of the anhydride and 25 cc. of absolute methyl alcohol with hydrogen chloride; the solid dissolved and after a day a new solid separated in the form of white needles. It was recrystallized from absolute methyl alcohol, in which it is sparingly soluble; m. p. 188°.

Anal. Calcd. for $C_{28}H_{28}O_8$: OCH_3, 25.5. Found: OCH_3, 25.3.

This work has been assisted by a grant from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences.

Summary

1. The structure of the bimolecular product resulting from the dehydration of anhydracetonebenzil has been determined. It is a tricyclic ring system, containing a carbonyl bridge.

2. One carbonyl group is lost as carbon monoxide on heating. The resulting product contains a conjugated system and easily adds maleic anhydride; it also forms thiophenol when heated with sulfur, and rearranges to an isomeric indanone.

3. When heated with sulfur, the indanone loses hydrogen sulfide and forms a red indone; the latter was degraded to *o*-diphenylbenzene.

4. Anhydracetonebenzil and excess maleic anhydride give a complex polycyclic dianhydride.

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[13] Burton and Shopee [*J. Soc. Chem. Ind.*, **51**, 981 (1932)] have criticized the mechanism suggested in the previous paper[3] for the formation of isomeric chlorides on the grounds that the possibility of an anionotropic change was disregarded, and cited as evidence the production of three isomeric dinitrophenylhydrazones for which they wrote three different structures. However, since Bredereck [*Ber.*, **65**, 1833 (1932)] has recently shown (1) that stereoisomeric 2,4-dinitrophenylhydrazones are possible, (2) that they are differently colored and (3) that the yellow, less stable form is readily isomerized to the red, stable form, the above evidence is inconclusive, especially as they had both yellow and red hydrazones. Further, β,β-dimethylanhydracetonebenzil does not give an isomeric chloride under the same conditions as the parent substance—this point was tested carefully—so that in view of these facts, as well as the production of the various addition products described in this paper, the assumption of an intermediate cyclopentadienone seems justified.