[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

The Structures of the Dimolecular Reduction Products of Dibenzoylethylene

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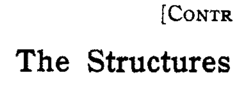
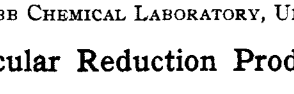
A dimolecular product has been obtained from the reduction of dibenzoylethylene (III) with the heterogeneous combination zinc and glacial acetic acid,[1] and further studies described in this and the two following papers have led to the isolation from the various reductions of a total of five isomers which are closely related structurally as is evident from the intertransformations described under Diagram 1. The results of our studies show that these five compounds are of two types. Two of them are *dl* and *meso* isomers of I and are designated for convenience as bis-dibenzoylethanes-A and -B. The other three appear to be cyclic internal ketols of these (II) and are named *cyclo*-bis-dibenzoylethanes-A, -B and -C.



$$\begin{array}{l} C_6H_5COCHCH_2COC_6H_5 \\ \quad\quad\quad | \\ C_6H_5COCHCH_2COC_6H_5 \end{array}$$

I



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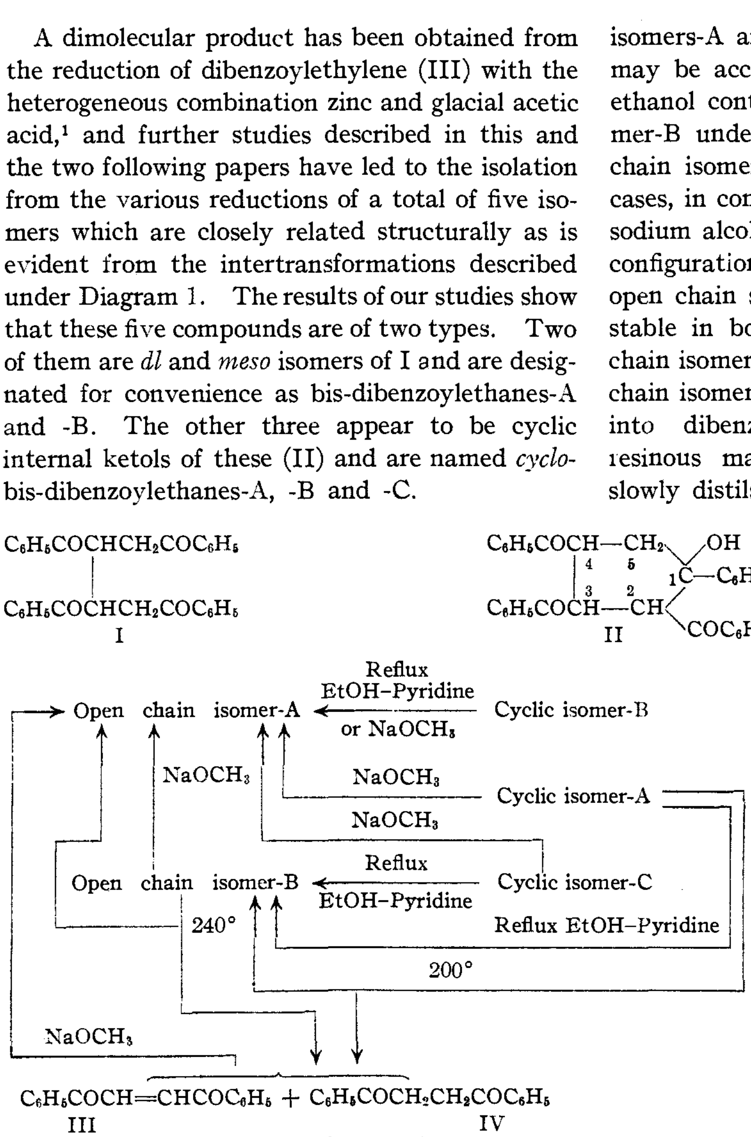

DIAGRAM 1.

All of these isomers are rearranged by sodium methylate into the open chain bis-dibenzoylethane-A which presumably separates from an equilibrium mixture through its exceeding insolubility in alcohol. In three of these transformations ring fission has taken place, presumably through reversal of an internal ketol condensation, and in at least two instances the configurations with respect to carbons 3 and 4 (formula II) have been reversed. The rearrangement of the cyclic isomers-A and -C into the open chain isomer-B may be accomplished also by refluxing in 85% ethanol containing pyridine; and the cyclic isomer-B under these conditions goes to the open chain isomer-A. The ring fissions in the latter cases, in contrast with those brought about with sodium alcoholate, take place without change in configuration, as is evident from the fact that both open chain stereoisomers are obtainable and are stable in boiling alcoholic pyridine. The open chain isomer-B is partly rearranged into the open chain isomer-A at 240° with some decomposition into dibenzoylethylene, dibenzoylethane and resinous materials; the open chain isomer-A slowly distils unchanged in the vacuum oven at this temperature. The cyclic isomers are unstable at temperatures above 200°; *cyclo*-bis-dibenzoylethane-A under these conditions is rearranged in excellent yield into the open chain isomer-B, accompanied by some decomposition giving small amounts of dibenzoylethylene and dibenzoylethane, III and IV.

It is very evident that the open chain isomers are the stable types and are formed easily by fission of the ring. The closure of the ring, however, has not been effected in any instance except during the actual formation of the dimolecular compounds in the reduction of dibenzoylethylene.

From the above facts it is clear that the configurations of the cyclic isomers-A and -C with respect to carbons 3 and 4 correspond to that of the open chain isomer-B, and the configuration of *cyclo*-B to that of the open chain isomer-A. The fact that, of the open chain isomers, A is the stable one (at 250°) and is the higher melting and the less soluble, suggests that possibly this is the *meso* form and that the isomer-B is *dl*,[2] and consequently that the cyclic isomer-B has the *cis* arrangement of

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[1] Lutz, THIS JOURNAL, **51**, 3008 (1929).

[2] *Cf.* the *dl*- and *meso*-dibenzoyldihalogenoethanes [Lutz, *ibid.*, **48**, 2905, 2916 (1926); **49**, 1106 (1927)] and the dihalogenosuccinic acids.

benzoyl groups on carbons 3 and 4, and -A and -C the *trans*.

All of the reactions and relationships described in Diagram 1 are consistent with the formulation of the dimolecular compounds either as open chain polyketones (I) or as cyclic internal ketols of these (II).

Dehydration either with acetic anhydride and sulfuric acid or with acetyl chloride was found to confirm the structures assigned above to the two types of dimolecular products. The open chain compounds, as diastereoisomeric bis-saturated 1,4-diketones, lose two molecules of water under these conditions and give one and the same bis-furan V whereas the cyclic isomers behave like β-hydroxy ketones and lose only one molecule of water, as would be expected from the formula II, to give the cyclic α,β-unsaturated ketone IX.

The dehydration of the open chain bis-dibenzoylethanes-A and -B is illustrated in Diagram 2. The structure of the product, bis-2,5-diphenylfuran V, is clear from the fact that upon oxidation with the nitric and glacial acetic acid reagent, a yellow compound is obtained which corresponds in analysis and properties with bis-dibenzoylethylene VI, and which is easily reduced by means of sodium hydrosulfite to bis-dibenzoylethane-A. The reactions involved are characteristic,[3] and constitute adequate evidence for the open chain formulation of the dimolecular compounds in question, particularly in view of the fact that the cyclic isomers behave consistently in a different sense.

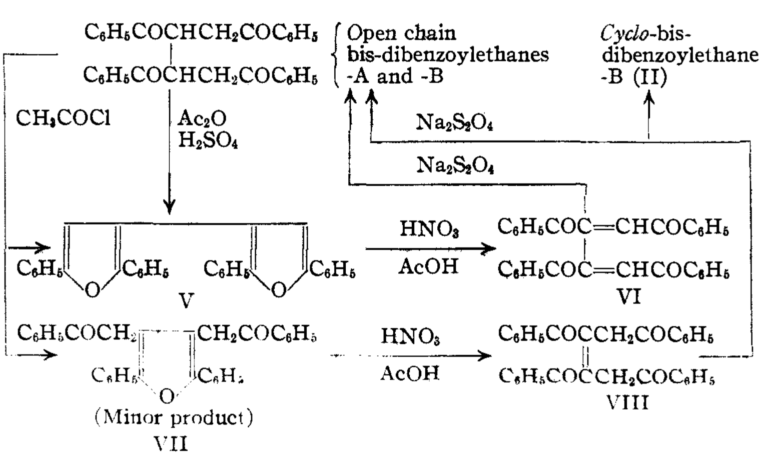

DIAGRAM 2.

A mono-dehydro compound, diphenacyldiphenylfuran (VII) theoretically could be formed also upon dehydration, since the open chain dimolecular compounds should be able to act also in the sense of the diphenacyl saturated 1,4-diketone. A search based on this consideration revealed such a product which was present in small amounts in the crude residues from the purification of the products of the dehydrations using acetyl chloride. This compound is oxidized by the nitric–glacial acetic acid reagent to a diphenacyldibenzoylethylene VIII (presumably the *cis* form), which in turn is reduced to a mixture of the dimolecular products by means of sodium hydrosulfite. These results are in complete accord with the various structures assigned in Diagram 2.

Bis-dibenzoylethane-A was synthesized by the direct condensation of dibenzoylethylene and dibenzoylethane by means of sodium methylate. This reaction (illustrated in Diagram 1) is analogous to the Michael condensation with α,β-unsaturated ketones and may be regarded as confirming the nature of the carbon chain in the dimolecular products. However, since all of the dimolecular compounds including the cyclic isomers are rearranged by means of sodium methylate into this same bis-dibenzoylethane-A, the reaction does not add further information concerning the isomerism. In connection with this reaction it is noteworthy that, whereas the condensation product is very stable and distils in high vacuum at 250°, the stereoisomeric bis-dibenzoylethane-B breaks down at this temperature, giving partly the more stable isomer-A (I) and also approximately equivalent amounts of dibenzoylethylene and dibenzoylethane, the products of a reversal of the Michael condensation.

The cyclic bis-dibenzoylethanes-A, -B and -C, in contrast with the open chain isomers, give on dehydration with acetic anhydride and sulfuric acid or with acetyl chloride only one product which is formed through the loss of one molecule of water and which is different from the diphenacylfuran obtained as described above. This characteristic reaction supports our formulation of the cyclic dimolecular compounds as substituted β-hydroxy ketones, and the dehydro compound as the cyclic

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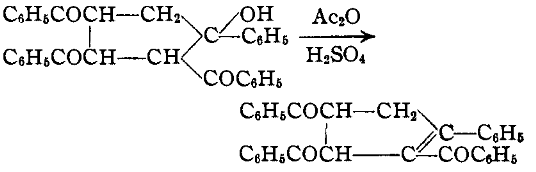
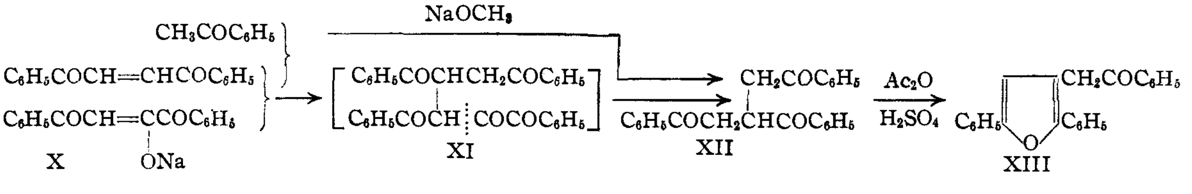
(3) *Cf.* Lutz and Wilder, THIS JOURNAL, 56, 978 (1934).

α,β-unsaturated ketone, 1-phenyl-2,3,4-tribenzoylcyclopentene, IX.[4] This hypothesis appears to be the only reasonable one available and is in complete accord with all of the facts.[5]


IX

Theoretically this dehydration product IX should exist in two diastereoisomeric forms, but only one has been obtained. Obviously in at least one instance reversal of configuration with respect to the groups about carbons 3 and 4 has occurred. The dehydro compound, unlike the true furans derived from I, does not react readily with the nitric–glacial acetic acid reagent under the usual conditions.

We had hoped through ozonization of this dehydro compound IX to accomplish fission of the ring and to obtain the pentaketone XI. We attempted to synthesize this pentaketone by the condensation of the sodium derivative of dibenzoylethenol and dibenzoylethylene. The reaction gave, however, tribenzoylpropane XII, a product clearly formed by hydrolytic cleavage of the desired and probably intermediate pentaketone. This hydrolytic product XII was synthesized also by the condensation of acetophenone and dibenzoylethylene, and its structure was confirmed by dehydration with acetic anhydride and sulfuric acid to the known phenacyldiphenylfuran XIII.[6]


X XI XII XIII

The ozonization of the cyclopentene IX did not proceed as expected, but nevertheless gave an ultimate result which was understandable and consistent with our formulation of the various compounds and reactions involved. The colorless compound obtained on hydrolysis of the noncrystalline product of ozonization proved to be a peroxide (XIV) from which the cyclopentene IX could be regenerated by gentle heating or by the action of potassium iodide, oxygen and iodine, respectively, being liberated. These reactions, particularly the latter, are typical of the peroxides of this type which are known.[7] Under the influence of sodium methylate the peroxide XIV is converted directly into tribenzoylpropane in small but significant yield; the reaction probably either involves rearrangement to the hypothetical pentaketone XI followed by hydrolytic fission, or proceeds through XV. The peroxide XIV when refluxed with 70% ethanol for twelve hours gave a new substance which according to analysis and molecular weight could be formed only through the loss of an atom of oxygen; this product must be the oxido compound of formula XV. The rearrangement with loss of oxygen of an α,β-peroxide to a β-diketone has been reported[8] but in the case in hand, since such a rearrangement is impossible without fission of the ring, it is not unreasonable to suppose that an oxide is formed. This compound under the influence of sodium methylate gives tribenzoylpropane XII in good yield. The reaction is accounted for in a reasonable way through a series of steps such as is illustrated in Diagram 3, namely, hydrolysis of the oxide system, ring fission involving a typical reversal of a ketol condensation (as in the change II $\xrightarrow{NaOCH_3}$ I), and hydrolytic splitting of the resulting product into tribenzoylpropane and phenylglyoxal (the latter would hardly be expected to be stable under the circumstances, and was not isolated).

While some of the steps in this degradation of the *cyclic* bis-dibenzoylethanes to tribenzoylpropane are not established with certainty, we believe nevertheless that the results constitute confirmatory evidence in support of the various structures assigned.

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(4) *Cf.* the internal condensation of the dimolecular reduction products of α,β-unsaturated ketones such as mesityl oxide, phorone, benzalacetone, and benzalacetophenone [Harries and Hübner, *Ann.*, **296**, 295 (1897); Harries and Eschenbach, *Ber.*, **29**, 2121 (1896); Conant and Cutter, THIS JOURNAL, **48**, 1016 (1926)].

(5) A hydroxydihydro-1,4-pyran formula for the cyclic dimolecular compounds is a possible but very improbable alternative to the cyclic ketol formulation because, while it might account for the stereoisomerism and some of the reactions, it involves a cyclic hemiacetal linkage between an enol hydroxyl and a carbonyl group, for which there is no analogy.

(6) Paal and Schulze, *Ber.*, **36**, 2435 (1903).

(7) *Cf.* Houben, "Die Methoden der organischen Chemie," Vol III, 1923, p. 254; Reiche, "Alkylperoxide und Ozonide," 1931, p. 71.

(8) *Cf.* Ref. 6, p. 257.

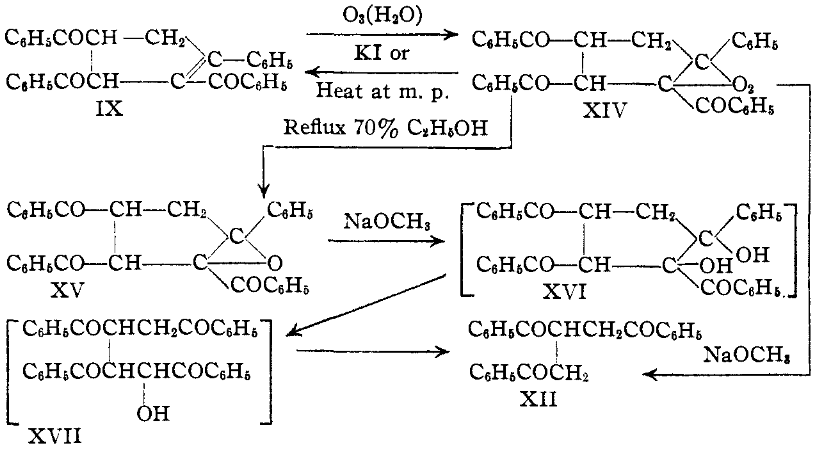

DIAGRAM 3.

Experimental Part

Bis-dibenzoylethane-A (1,6-diphenyl-3,4-dibenzoyl-hexanedione-1,6), I, is best prepared by the condensation of dibenzoylethane and dibenzoylethylene. A suspension of 2 g. of dibenzoylethane in 125 cc. of absolute ethanol was treated with a solution of 0.25 g. of sodium in 30 cc. of absolute ethanol, and the resulting mixture added with stirring over a period of three hours to a suspension of 2 g. of dibenzoylethylene in 100 cc. of absolute ethanol. The solids dissolved and a fine crystalline precipitate appeared. On standing for two hours, 2.5 g. of nearly pure product was obtained (yield 62%). It crystallized as short prisms from chloroform (adding a little petroleum ether) and from chlorobenzene; m. p. 202° (corr.). The method works equally well on a larger scale, and with methanol as the solvent. The compound is very difficultly soluble in hot ethanol (about 0.15 g. per 100 cc. at the boiling point), and acetone.

Anal. Calcd. for $C_{32}H_{26}O_4$: C, 81.01; H, 5.48. Found: C, 80.79; 80.66; H, 5.47; 5.69.

This isomer may also be prepared as follows: (a) 1 g. of *cyclo*-bis-dibenzoylethane-A was shaken with 100 cc. of absolute ethanol containing 0.4 g. of dissolved sodium. On standing for fifteen hours the crystalline precipitate was filtered from the red solution (0.2 g.), was recrystallized from chlorobenzene, and identified as bis-dibenzoylethane-A by mixed m. p. (b) A mixture of *cyclo*-bis-dibenzoylethane-B (0.01 g.) in 2 cc. of ethanol with 1 drop of pyridine was refluxed for twenty-four hours and deposited a cake of the characteristic granular crystals of the open chain bis-dibenzoylethane-A (identified by mixed m. p.).

This isomer is unaffected by fusion at 240–250° in the vacuum oven and distils slowly onto the cold finger condenser with a slight amount of decomposition. It is unaffected by prolonged refluxing in chlorobenzene or ethanol.

Bis-dibenzoylethane-B (1,6-diphenyl-3,4-dibenzoyl-butanedione-1,6), I, is formed in small amounts in some of the reductions described in the following two papers, but it is difficult to isolate since it is the most soluble of the five dimolecular compounds. It is best prepared by rearrangement of *cyclo*-bis-dibenzoylethane-A in either of the following two ways: (a) a mixture of 5 g. of *cyclo*-bis-dibenzoylethane-A, 280 cc. of 85% ethanol, and 3.4 g. of pyridine was refluxed for twenty-four hours. On cooling and filtering 2.4 g. of nearly pure open chain isomer-B was obtained. A second crop was obtained from the filtrate (total yield 65–75%). (b) *Cyclo*-bis-dibenzoylethane-A was fused at 200° in the vacuum oven for one hour, giving a small amount of distillate which collected on the cold finger condenser (this was shown to be a mixture of approximately equal amounts of dibenzoylethane and dibenzoylethylene which were isolated and identified by mixed melting points). The fused mass, on crystallization from alcohol, proved to be nearly pure bis-dibenzoylethane-B. This isomer was obtained also as follows: 0.05 g. of *cyclo*-bis-dibenzoylethane-C was refluxed in 5 cc. of 95% ethanol with 4 drops of pyridine for twenty-one hours. On dilution with water 0.04 g. of nearly pure bis-dibenzoylethane-B was obtained and identified.

The compound crystallizes as characteristic thin square plates from ethanol; m. p. 168° (corr.).

Anal. Calcd. for $C_{32}H_{26}O_4$: C, 81.01; H, 5.48. Found: C, 80.84, 80.75; H, 5.49, 5.47.

The compound is not affected by long refluxing in ethanol.

Pyrolysis and distillation of 1 g. in the vacuum oven at 230–240° gave a distillate containing some bis-dibenzoylethane-A and considerable amounts of dibenzoylethane and dibenzoylethylene (identified by mixed melting points).

Rearrangement.—A solution of 0.07 g. in 5 cc. of methanol containing 0.05 g. of dissolved sodium, on standing for twenty-four hours, gave a crystalline deposit of the open chain isomer-A (0.05 g., identified by mixed m. p.).

3,3′-Bis-2,5-diphenylfuran, V.—Ten grams of bis-dibenzoylethane-A (or -B) was suspended in 50 cc. of acetic anhydride and 10–15 drops of concd. sulfuric acid. The resulting solution on standing for fifteen minutes was decomposed in ice water, giving 7.1 g. of nearly pure product which was crystallized from acetone; m. p. 195–196° (corr.).

Anal. Calcd. for $C_{32}H_{22}O_2$: C, 87.67; H, 5.02. Found: C, 87.57, 87.67; H, 5.08, 5.08.

One-gram samples of both isomers, I-A and I-B, on standing for eighteen hours in 50 cc. of acetyl chloride, with subsequent hydrolysis, gave mixtures consisting largely of the bis-diphenylfuran. The crude product was washed with hot alcohol, leaving the bis-furan as the residue; the washings contained the diphenacylfuran which is described below.

Bis-1,2-dibenzoylethylene (1,6-Diphenyl-3,4-dibenzoyl-2,4-hexadiene-1,6-dione), VI.—Ten grams of V was suspended in 75 cc. of glacial acetic acid and a solution of 5 cc. of concd. nitric acid in 25 cc. of glacial acetic acid was added slowly, the temperature maintained at 30–35°. The crystals went into solution and a yellow solid then separated. After ten minutes this was filtered; yield 6.3 g. of m. p. 205–210°. It was recrystallized from chloroform–acetone mixtures and from butanone; m. p. 214–218° (corr.).

Anal. Calcd. for $C_{32}H_{22}O_4$: C, 81.67; H, 4.72. Found: C, 81.61; H, 4.79.

Reduction of 0.5 g. with 3 g. of sodium hydrosulfite in 100 cc. of 70% ethanol (refluxing two hours) gave 0.24 g. of bis-dibenzoylethane-A (identified by mixed melting point). Catalytic reduction (platinum) in ethyl acetate was stopped when the reaction rate slowed down with the absorption of approximately one molecule of hydrogen, but gave largely non-crystalline products and a small yield of bis-dibenzoylethane-A. Zinc and glacial acetic acid reduction appeared to give two new products (*cf.* m. p. 160–165° and 199–200°) which have not yet been investigated.

2,5-Diphenyl-3,4-diphenacylfuran, VII.—The residue from evaporation of the alcohol washings from the main fractions in the above-described dehydration of the open chain bis-dibenzoylethanes with acetyl chloride, was fractionally crystallized from ethanol and gave a very small amount of the second product which melted at 164–165° (corr.).

Anal. Calcd. for $C_{32}H_{24}O_3$: C, 84.17; H, 5.31. Found: C, 84.10; H, 5.51.

(*Cis*)-1,2-diphenacyl-1,2-dibenzoylethylene (1,6-Diphenyl-3,4-dibenzoyl-3-hexene-1,6-dione) VIII.—A suspension of 0.1 g. of VII in 0.7 cc. of glacial acetic acid was treated with 0.05 cc. of concd. nitric acid in 0.25 cc. of glacial acetic acid. Immediate reaction at room temperature took place, a new crystalline product appearing. After standing ten minutes, cooling, and filtering, 0.085 g. of nearly pure product was obtained which, after several crystallizations from ethanol, melted at 183–184° (corr.).

Anal. Calcd. for $C_{32}H_{24}O_4$: C, 81.31; H, 5.12. Found: C, 81.19; H, 5.17.

Reduction of 0.016 g. with 2 g. of sodium hydrosulfite in 2 cc. of 70% ethanol (refluxing fifteen minutes) gave 0.015 g. of a mixture of bis-dibenzoylethanes melting at 182–183° which showed a mixed melting point depression with *cyclo*-bis-dibenzoylethane-C, but none with the cyclic isomer-B and the open chain isomer-A. The microscopic examination of the crystals indicated that the product is really the mixture of the latter two isomers as shown by the mixed melting points.

1-Phenyl-2,3,4-tribenzoylcyclopentene-1, IX.—Ten grams of *cyclo*-bis-dibenzoylethane-A was dissolved in 75 cc. of acetic anhydride at 90° and 8 drops of concd. sulfuric acid added, the mixture then being heated for twenty minutes at 90° and decomposed in ice water. On completion of hydrolysis the solid was precipitated nearly pure and was filtered and washed with water; yield 8.1 g. It crystallized from ethanol as large thin rhombic needles; m. p. 182° (corr.).

Anal. Calcd. for $C_{32}H_{24}O_3$: C, 84.17; H, 5.31. Found: C, 84.10, 84.09; H, 5.34, 5.31.

The 1-Phenyl-2,3,4-tribenzoylcyclopentene-1 Peroxide, XIV.—Ozonized oxygen was passed for four hours through a solution of 5 g. of IX in 30 cc. of dry chloroform. The solvent was then evaporated in a current of moist air and the residue allowed to stand in contact with water. The product was extracted with ether, and on concentrating a total of 3.5 g. of crystals was isolated; m. p. 115–118° (with effervescence). Recrystallization from chloroform–ether or ethyl acetate–ligroin mixtures gave the m. p. 132–133° (corr.) (with effervescence). Alcohol was not used for recrystallization since decomposition occurs in this solvent. Attempts to induce the oily ozonide to crystallize were unsuccessful, and digestion with water appeared necessary to obtain a crystalline product. Ozonization carried out in 80% glacial acetic acid gave directly the peroxide.

Anal. Calcd. for $C_{32}H_{24}O_5$: C, 78.66; H, 4.95. Found: C, 78.38; H, 4.88.

Pyrolysis of the peroxide by heating slowly to 140° gave a fused mass from which on crystallization from ethanol only IX was obtained (identified by mixed melting point). When pyrolysis was effected by sudden heating of the sample in an oil-bath at 140–150°, violent evolution of gas occurred with deposition of benzoic acid on the walls of the vessel. Crystallization of the residue from acetone gave a new substance of m. p. 217–219° (corr.) which gave the analysis, C, 82.52; H, 5.28; and molecular weight (Rast) 308, 291.

The action of potassium iodide in ethanol on the peroxide liberated free iodine and regenerated IX which was identified by mixed melting point.

Hydrolysis of 0.5 g. with 10 cc. of methanol containing 0.05 g. of dissolved sodium (standing twenty-four hours) gave a red solution from which 0.1 g. of tribenzoylpropane crystallized and was identified by mixed melting point.

1-Phenyl-2,3,4-tribenzoyl-1,2-epoxycyclopentane, XV.—Two grams of the peroxide XIV, on refluxing in 75 cc. of 70% ethanol for twelve hours, gave 1.35 g. of a new product which on repeated crystallization from butanone and from methanol (containing a little acetone) was obtained as thin rectangular scales of m. p. 117–119° (corr.) (a mixed melting point with the peroxide gave a sharp depression).

Anal. Calcd. for $C_{32}H_{24}O_4$: C, 81.31; H, 5.12; mol. wt. 472. Found: C, 81.48, 81.50; H, 5.35, 5.35; mol. wt. (freezing point in benzene), 450.

Hydrolysis of 0.5 g. in 10 cc. of methanol containing 0.05 g. of dissolved sodium (standing one week) gave a red solution from which 0.24 g. of solid crystallized. The product was washed with ethanol and identified by melting point (120–121°) and mixed melting point as tribenzoylpropane. From the filtrates 0.03 g. of benzoic acid was isolated.

Acetic anhydride containing concd. sulfuric acid reacts with the oxide to give a deep indigo-blue solution from which, even after refluxing, the oxide is recovered on hydrolysis.

Tribenzoylpropane (1,4-Diphenyl-2-phenacyl-1,4-butanedione), XII.—The structure of the true tribenzoylpropane is evident from the mode of formation and dehydration to the furan as described in the foregoing discussion.

The product obtained by the Friedel and Crafts reaction on tricarballylic acid chloride[9] (XVIII) and supposed without evidence to be tribenzoylpropane, is different from our compound the structure of which is certain

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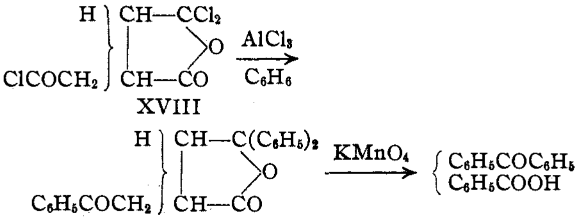
[9] Emery, *Ber.*, **24**, 601 (1891).

from the above data. Since it is an isomer, this product must be either α- or β-phenacyl-γ,γ-diphenylbutyro-γ-lactone (XIX), a structure which finds strong support from the following facts; with phenylhydrazine only a monophenylhydrazone is formed[6] and on oxidation with alkaline permanganate approximately equivalent amounts of benzophenone and benzoic acid are produced.



XVIII

XIX

Tribenzoylpropane (1,4-Diphenyl-2-phenacyl-1,4-butanedione) XII.—Three grams each of dibenzoylethanol and dibenzoylethylene were added to a solution of 0.3 g. of sodium in 30 cc. of methanol. On standing for twenty-four hours the substances dissolved and new crystals deposited. On cooling 1.3 g. of product was obtained which after repeated crystallization from ethanol melted at 122° (corr.). When the equivalent amount of the sodium salt of dibenzoylethanol was substituted in the reaction for the free enol and sodium methylate, the yield was raised to 50–60%. A third procedure is as follows: 2 g. of dibenzoylethylene in 25 cc. of methanol and 1.8 g. of acetophenone was treated with 0.2 g. of sodium dissolved in methanol. After several hours 0.5 g. of tribenzoylpropane crystallized.

Anal. Calcd. for $C_{24}H_{20}O_3$: C, 80.86; H, 5.66. Found: C, 80.51, 80.84; H, 5.61, 5.66.

Conversion into the known 2,5-diphenyl-3-phenacylfuran XIII was accomplished as follows: 0.2 g. of XII was dissolved in hot acetic anhydride containing one drop of concd. sulfuric acid. On decomposition with water 0.15 g. of diphenylphenacylfuran crystallized (m. p. 115–116° after repeated crystallization from ethanol [Paal and Schulze[6] reported 113°]). This product when treated with 40% hydrazine hydrate gave the characteristic ketazine melting at 214–215° (*cf.* Ref. 5).

α- or β-Phenacyl-γ,γ-diphenylbutyro-γ-lactone, XIX, (the so-called tribenzoylpropane of Emery[9]) was prepared from tricarballylic acid chloride exactly as described by Emery[9] in a yield of 48% (the rest of the material was an intractable resin). It gave a sharp mixed melting point depression with the true tribenzoylpropane XII described above. Tricarballylic acid chloride is hydrolyzed by water on standing for several hours, the acid being regenerated. A sample of the lactone XIX was suspended in alkaline permanganate (excess) and the mixture distilled. Pure benzophenone was obtained in the steam distillate in a yield of 50%. A similar yield of benzoic acid was recovered from the residual mixture.

Summary

The intertransformations and relationships of the five isomeric dimolecular reduction products of dibenzoylethylene are described. Two are open chain compounds and three are cyclic internal ketols.

Evidence for the open chain structures involves dehydration to mono- and bis-furans, oxidation to the unsaturated 1,4-diketone types, and reduction again to the original compounds. One of the open chain isomers was synthesized by condensation of dibenzoylethylene and dibenzoylethane.

The dehydration of the cyclic isomers gives a cyclic α,β-unsaturated ketone which is degraded by ozonization, through a peroxide and an oxide to tribenzoylpropane which was synthesized by condensation of acetophenone and dibenzoylethylene. The interpretation of these reactions and the bearing on the problem of structure is considered.

The product of the Friedel–Crafts reaction on tricarballylic acid chloride is shown to be a phenacyl-γ,γ-diphenylbutyro-γ-lactone.

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