[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

2,3-Dibenzoylpropene. The Addition of Hydrogen Chloride to 1,2-Dibenzoylpropene[1]

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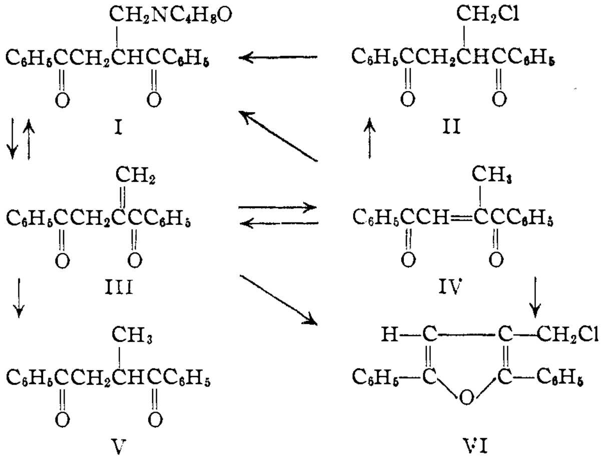
2,3-Dibenzoylpropene has been synthesized and its assumed role as an intermediate in the reaction between 1,2-dibenzoylpropene and amines to give 3-amino-1,2-dibenzoylpropanes has been demonstrated. Hydrogen chloride has been shown to add to 1,2-dibenzoylpropene to give 3-chloro-1,2-dibenzoylpropane and 3-(chloromethyl)-2,5-diphenylfuran. Improved preparations of mesaconyl chloride and *trans*-1,2-dibenzoylpropene are reported.

In order to test the assumed role of 2,3-dibenzoylpropene (III) as an intermediate in the reaction between the 1,2-dibenzoylpropenes (IV) and amines to give 3-amino-1,2-dibenzoylpropanes such as I[3] we have prepared and characterized this substance and have studied its equilibration with IV using triethylamine.

2,3-Dibenzoylpropene (III) along with 3-(4-morpholinylmethyl)-2,5-diphenylfuran hydrochloride and some 1,2-dibenzoylethane[4] results when an aqueous solution of the hydrochloride of 1,2-dibenzoyl-3-(4-morpholinyl)-propane (I) is refluxed. Its structure has been established by reduction to 1,2-dibenzoylpropane (V) and by ozonolysis to formaldehyde. Neither *cis*- nor *trans*-1,2-dibenzoylpropene give appreciable amounts of formaldehyde upon ozonolysis. 2,3-Dibenzoylpropene (III) adds morpholine to give I and reacts with hydrogen chloride to give the known 3-(chloromethyl)-2,5-diphenylfuran (VI). It forms a different dioxime than does either of the 1,2-dibenzoylpropenes (IV).

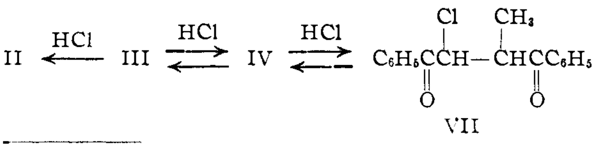


The action of triethylamine on *trans*-1,2-dibenzoylpropene (IV), reported earlier to yield the *cis*-isomer,[3] has now been shown to yield a mixture of this substance and 2,3-dibenzoylpropene (III) as evidenced by infrared data, by the isolation of the dioxime of the *cis*-compound and by the formation of formaldehyde upon ozonolysis. The percentage yield of formaldehyde was 16% as compared with 47% from the supposedly pure 2,3-dibenzoylpropene (III) and 3–4% from the pure *cis*- and *trans*-1,2-dibenzoylpropenes (IV). The ozonolysis of the crude products from triethylamine reactions with III and the *cis*-isomer of IV also gave intermediate formaldehyde yields of 13 and 23%, indicating the establishment of an equilibrium between these two substances upon treatment of either (or the *trans*-isomer) with triethylamine. This demonstration supports the reaction scheme proposed earlier for the interaction of amines and the 1,2-dibenzoylpropenes (IV).[3]

A study of the infrared spectra of III, the *cis* and *trans* isomers of IV, and the several times recrystallized product from the triethylamine *trans*-IV reactions (Fig. 1)[5] indicates that the 2,3-dibenzoylpropene (III) is probably contaminated with 5–10% of *cis*-1,2-dibenzoylpropene (IV). For example, compare the percentage transmission of the bands at 9.5 and 11.7 microns. Likewise, it is evident that the purified material from the triethylamine reaction contains a large amount of the *cis*-isomer of IV.

The ease with which 2,3-dibenzoylpropene (III) reacted with hydrogen chloride suggested a study of the behavior of the 1,2-dibenzoylpropenes (IV) with this reagent. The reactions of both isomers were analogous to their reactions with amines. In a fairly concentrated ethereal hydrogen chloride solution the product was 3-chloro-1,2-dibenzoylpropane (II) while in a saturated chloroform–hydrogen chloride or saturated ethereal hydrogen chloride solution the product was VI. Evidence for the structure assigned to II was its cyclization to VI by means of a saturated chloroform–hydrogen chloride solution and its reaction with morpholine to give I.

Earlier, Lutz and Stuart found that IV reacted with hydrogen bromide in the presence of acetic acid, acetic anhydride and sulfuric acid to give 3-bromo-4-methyl-2,5-diphenylfuran.[6] The difference in their results and ours most probably means that in the hydrogen halide reactions there are two competing additions. The first is a fast reversible reaction to give the relatively unstable VII (or the corresponding bromo compound) and the other



$$\mathrm{II} \xleftarrow{\mathrm{HCl}} \mathrm{III} \underset{}{\overset{\mathrm{HCl}}{\rightleftarrows}} \mathrm{IV} \overset{\mathrm{HCl}}{\rightleftarrows} C_6H_5\underset{\underset{O}{\|}}{C}CH-\overset{\overset{CH_3}{|}}{C}HC\!\!\underset{\underset{O}{\|}}{}C_6H_5$$

VII

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[1] This is the sixth communication concerning 1,3-hydrogen shifts in reactions of dibenzoylalkenes and related compounds. For the fifth see P. S. Bailey, E. E. Kawas and L. L. Smith, THIS JOURNAL, 73, 4088 (1951).

[2] Taken in part from the Ph.D. dissertation of Gene Nowlin, May, 1949, and the M.A. thesis of J. V. Waggoner, January, 1950.

[3] R. E. Lutz and P. S. Bailey, THIS JOURNAL, 67, 2229 (1945).

[4] The formation of 1,2-dibenzoylethane is interesting in that it apparently constitutes a reverse Mannich reaction.

[5] These spectra were run by Samuel P. Sadtler and Son, Inc., of Philadelphia, Pennsylvania. The tracings were by Mr. C. L. Wimberley of The University of Texas.

[6] R. E. Lutz and A. H. Stuart, THIS JOURNAL, 59, 2316 (1937).

is a slow reaction involving isomerization and addition to III to give the more stable product II. The strongly furanizing conditions of Lutz and Stuart[4] probably caused cyclization of the bromo analog of VII before the competing reactions could occur. The assumed instability of VII is reasonable in view of the ease with which 1-bromo and 1-chloro-1,2-dibenzoylethanes split out hydrogen halide to regenerate 1,2-dibenzoylethylene.

In an earlier paper the reaction of 2,3-dibenzoyl-1-(4-morpholinyl)-2-butene with hydrochloric acid followed by neutralization with sodium carbonate to give 3-(hydroxymethyl)-4-(4-morpholinylmethyl)-2,5-diphenylfuran was described.[7] The assumed intermediate, 3-(chloromethyl)-4-(4-morpholinylmethyl)-2,5-diphenylfuran hydrochloride, has now been isolated, showing that the reaction is analogous to the conversion of IV to VI.

In the experimental section of this paper improved preparations of mesaconyl chloride and *trans*-1,2-dibenzoylpropene (IV) are described.

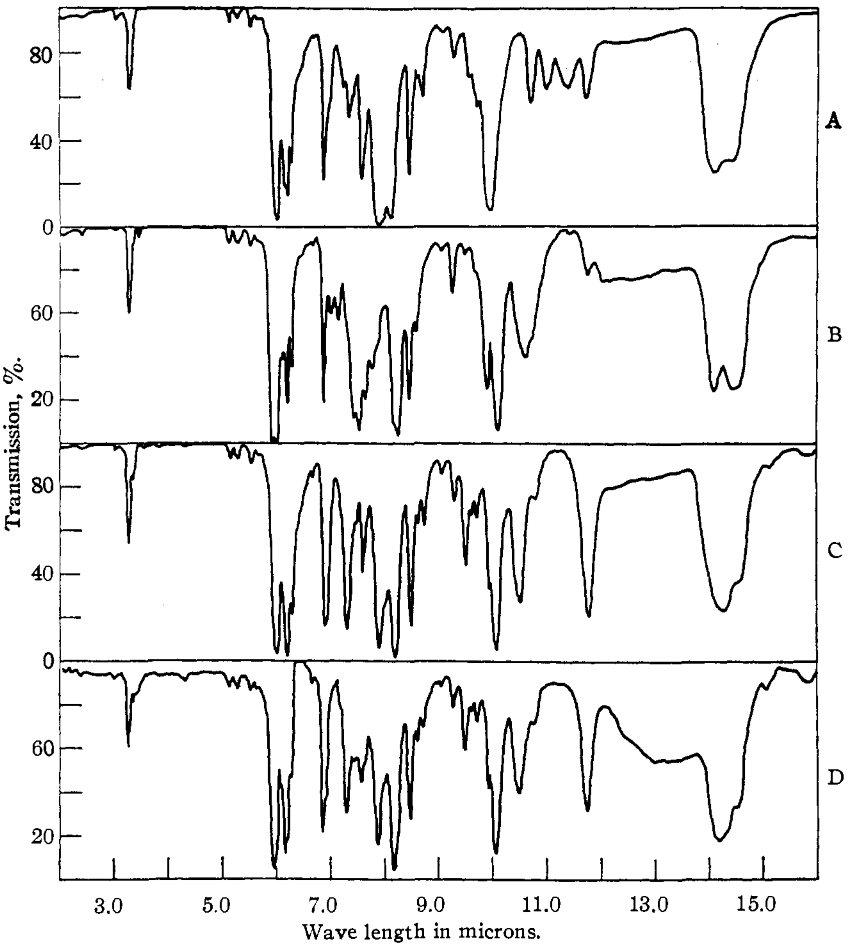

Fig. 1.—Infrared spectra of: A, *trans*-1,2-dibenzoylpropene; B, 2,3-dibenzoylpropene; C, *cis*-1,2-dibenzoylpropene; D, recrystallized product from triethylamine-1,2-dibenzoylpropene reaction. Baird spectrophotometer with NaCl prism. Solutions of 100 mg. in 1.0 ml. of carbon tetrachloride.

Experimental[8]

Mesaconyl chloride[9] was prepared by an improved procedure analogous to the preparation of fumaryl chloride.[10] A solution of 120 g. of citraconic anhydride,[11] 247 g. of phthalyl chloride and 2 g. of fused zinc chloride was heated for three hours at 127–130°, distilled over ten hours through a 12-in. Vigreux column at 10 mm. pressure, and fractionated through a Snyder column at 5 mm.; 99 g. (55%); b.p. 48–49°; $n^{20}\mathrm{D}$ 1.5040. The material yielded mesaconic acid[12] upon hydrolysis.

***trans*-1,2-Dibenzoylpropene**[13] (IV) was prepared in improved yield by the slow addition of 40 g. of mesaconyl chloride to a stirred mixture of 250 ml. of dry benzene and 75 g. of reagent grade, anhydrous aluminum chloride, with continued refluxing for one hour after the addition; crystallized from ethanol, 54 g. (90%); m.p. 51–53°.

2,3-Dibenzoylpropene (III).—Eighteen grams of I[3] was treated with dilute hydrochloric acid until exactly neutralized. The resulting solution (150 ml.) was refluxed for several hours during which time an oil precipitated. The oil was extracted with ether every hour and the aqueous layer was heated in the open to remove dissolved ether before the refluxing was continued. Evaporation of the combined ether extracts and crystallization of the residue from ethanol gave 6.8 g. of material melting at 46–58°. From the aqueous layer was obtained upon cooling, 0.6 g. (3%) of 3-(4-morpholinylmethyl)-2,5-diphenylfuran hydrochloride (m.p. 215–223°). Evaporation of the filtrate and crystallization of the residue from ethanol gave a gummy solid (5.3 g.) which was shown to be the hydrochloride of I by conversion to I (m.p. 83–84°) with sodium carbonate. Recrystallization of the 46–58° material from ethanol gave a 2% yield of 1,2-dibenzoylethane (m.p. 144–145°) and a 30% yield of 2,3-dibenzoylpropene (m.p. 54–60°); analytical sample (ethanol) 59.8–60°. The known materials were identified by the mixture melting point method.

Anal. Calcd. for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.54, 81.18; H, 5.76, 5.60.

Dioxime crystallized with difficulty from 50–60% ethanol; m.p. 201–202°.

Anal. Calcd. for $C_{17}H_{16}N_2O_2$: C, 72.84; H, 5.75; N, 9.99. Found: C, 72.33; H, 5.73; N, 9.87, 9.81.

Reduction to V was carried out in 95% yield (m.p. 102–104°) by the method which Lutz and Taylor[14] used to reduce the *trans*-isomer of IV.

Conversion to I was performed in 76% yield (m.p. 83–84°) by the same method used previously with IV.[3] Identifications were by the mixture melting point method.

Ozonolyses of III and the *cis*- and *trans*-isomers of IV were carried out in an ice-bath using 1–2-g. samples in 50 ml. of C.P. ethyl acetate. Five to six per cent. ozone was

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[7] P. S. Bailey and G. Nowlin, This Journal, **71**, 732 (1949).

[8] The melting points reported here are corrected. Some of the microanalyses were performed by the Clark Microanalytical Laboratory of Urbana, Illinois.

[9] Petri, *Ber.*, **14**, 1635 (1881).

[10] L. P. Kyrides in C. F. H. Allen, "Organic Syntheses," Vol. 20, John Wiley and Sons, Inc., New York, N. Y., 1940, p. 51.

[11] R. L. Shriner, S. G. Ford and L. J. Roll in A. H. Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 140.

[12] R. L. Shriner, S. G. Ford and L. J. Roll, *ibid.*, p. 382.

[13] R. C. Fuson, C. L. Fleming and R. Johnson, This Journal, **60**, 1994 (1938).

[14] R. E. Lutz and R. J. Taylor, *ibid.*, **55**, 1177 (1933).

passed through for about 100 min. per 1 g. of sample at the rate of 3 l. per hour. Both the incoming and outgoing streams were analyzed to ensure the use of 150% excess ozone (this value was found to give the best results upon test runs with itaconic acid). The outgoing ozone stream was passed through a water trap. The ozonide was decomposed by cold water (from the trap) and zinc dust, after which the ethyl acetate was extracted several times with small amounts of water. The combined extracts gave 47, 3 and 4% yields of formaldehyde–dimedone derivative (m.p. 180–190°, no depression in admixture with a known sample) for III and the *cis* and *trans* isomers of IV, respectively.

Dioxime of *cis*-1,2-dibenzoylpropene crystallized with difficulty from 50–60% ethanol; m.p. 145–146°.

Anal. Calcd. for $C_{17}H_{16}N_2O_2$: C, 72.84; H, 5.75; N, 9.99. Found: C, 73.12; H, 5.90; N, 9.80.

Dioxime of *trans*-1,2-dibenzoylpropene was made by the pyridine method.[15] Crystallized with difficulty from 50–60% ethanol, m.p. 171–172°.

Anal. Calcd. for $C_{17}H_{16}N_2O_2$: C, 72.84; H, 5.75; N, 9.99. Found: C, 72.73; H, 6.04; N, 9.91.

Equilibration of IV and III with Triethylamine.—Upon evaporation of a solution of 5 g. of the *trans*-isomer of IV, 25 ml. of triethylamine and 60 ml. of ether, which had stood for 24 hours, 2.2 g. of material melting at 55–58° was obtained (crystallized from ethanol; after several recrystallizations m.p. 59–60°, no depression in a mixture melting point with III).[16] Treatment with hydroxylamine gave a small amount of the dioxime of the *cis*-isomer of IV (m.p. 135–140°, identified by mixture melting point method). Ozonolysis of the crude material by the procedure described earlier gave a 16% yield of the formaldehyde–dimedone derivative. Similar experiments with the *cis*-isomer of IV and with III gave 23 and 13% yields of the formaldehyde–dimedone derivative, respectively.

Hydrogen Chloride Additions (a) With 2,3-Dibenzoylpropene (III).—A solution of 1 g. of III in 50 ml. of saturated chloroform–hydrogen chloride was allowed to stand for 36 hours after which it was evaporated and the residue was crystallized from isopropyl alcohol (1 g. of colorless crystals, 93%, m.p. 58–64°). A pure sample, from isopropyl alcohol, melted at 69–70°. The compound was identified as VI (earlier the melting point was reported as 62–63°[17]) by its conversion, with morpholine, to 3-(4-morpholinylmethyl)-2,5-diphenylfuran (m.p. of hydrochloride, 218–220°, no depression in admixture with a known sample[3]).

(b) With *cis*- and *trans*-1,2-Dibenzoylpropene (IV).—When the reactions were carried out exactly as described with III in the preceding experiment except that the solution was resaturated with hydrogen chloride one or two times during the reaction period, yields up to 86% of VI were obtained (m.p. 68–70°, no melting point depression in admixture with known sample). When the reaction was carried out in saturated ethereal hydrogen chloride (dry gas passed at 0° for five hours) similar yields of VI were obtained.

3-Chloro-1,2-dibenzoylpropene (II) resulted in 80% yield (m.p. 96–97°) however, when the reactions were carried out in ethereal hydrogen chloride which was treated with dry gas at 0° for only one hour. An analytical sample (from isopropyl alcohol) melted at 97–97.5°.

Anal. Calcd. for $C_{17}H_{15}ClO_2$: C, 71.27; H, 5.27. Found: C, 71.59, 71.67; H, 5.44, 5.82.

Upon reaction with saturated chloroform–hydrogen chloride II gave VI (m.p. 69–70°, no depression in a mixture melting point with a known sample). Also, II was converted to I upon treatment with morpholine in dry ether solution (m.p. 82–83°, no depression in mixture melting point with known sample).

Reaction of Hydrochloric Acid with 2,3-Dibenzoyl-1-(4-morpholinyl)-2-butene.—A solution of 0.5 g. of *cis*-2,3-dibenzoyl-1-(4-morpholinyl)-2-butene in 20 ml. of 6 *N* hydrochloric acid was set aside for two hours after which time it was evaporated under reduced pressure and the residue was crystallized from acetone (0.3 g., m.p. 215–218°; after additional recrystallizations, m.p. 228–230°). The substance was identified as 3-(chloromethyl)-4-(4-morpholinylmethyl)-2,5-diphenylfuran hydrochloride by a mixture melting point with a known sample[7] and by conversion to 3-(hydroxymethyl)-4-(4-morpholinylmethyl)-2,5-diphenylfuran[7] simply upon treatment with aqueous sodium carbonate (m.p. 173–174°, no depression in a mixture melting point with a known sample.)

Dehydrohalogenation of 1-Chloro-1,2-dibenzoylethane.—A mixture of 0.75 g. of 1,2-dibenzoyl-1-chloroethane, 5 ml. of triethylamine and 10 ml. of dry ether was set aside for 12 hours after which the triethylamine hydrochloride was filtered off, the filtrate was evaporated by a stream of air, and the residue was crystallized from ethanol (0.4 g. of 1,2-dibenzoylethylene, crytallized from ethanol, m.p. 109–111°, no depression in a mixture melting point with a known sample). Similar results were obtained with 1,2-dibenzoyl-1-bromoethane. When the reaction was tried with 3-chloro-1,2-dibenzoylpropane (II) for 36 hours, a 75% recovery of starting material was obtained.

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[15] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," 2nd Ed., John Wiley and Sons, Inc., New York, N.Y., 1940, p. 167.

[16] A similar material was obtained from a few nitric acid oxidations of 3-methyl-2,5-diphenylfuran following the procedure of R. E. Lutz and C. E. McGinn, This Journal, **64**, 2585 (1942), with the exception that the solution of furan was poured into the nitric acid solution. Reproducible results could not be obtained, however.

[17] P. S. Bailey and R. E. Lutz, This Journal, **67**, 2232 (1945).