Further Reactions of 1,2-Dibenzoylethylene[1]

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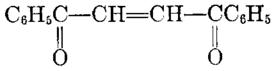
Incidental to recent studies with 1,2-dibenzoylpropene[2] it has been found that sodium bisulfite, malonic ester, *n*-butyl and *n*-amyl mercaptan, and hydrogen cyanide do not give tractable addition products. The first three of these reagents, however, were added successfully to 1,2-dibenzoylethylene (I).

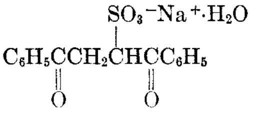
The bisulfite addition compound of dibenzoylethylene (I)[3] has now been obtained in pure form and shown to exist as the monohydrate (II). It was stable to boiling 10% hydrochloric acid for four hours, showing that it was not the product of 1,2-addition.

Although the Michael reaction between *trans*-1,2-dibenzoylethylene (I) and diethyl benzylmalonate has been reported,[4] the authors have found no record of the reaction with diethyl malonate itself. In the present research the addition product (IIIa) was obtained in good yield using piperidine catalyst. It was readily hydrolyzed in good yield to the corresponding diacid (IIIb) which underwent decarboxylation in quantitative yield to β,γ-dibenzoylbutyric acid (IV).



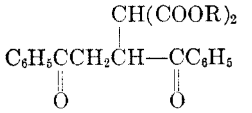
$C_6H_5C(=O)—CH=CH—C(=O)C_6H_5$

I



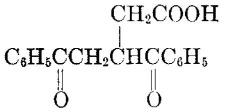
$C_6H_5C(=O)CH_2CH(SO_3^-Na^+\cdot H_2O)C(=O)C_6H_5$

II



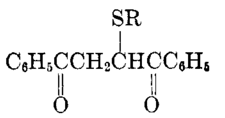
$C_6H_5C(=O)CH_2CH(CH(COOR)_2)—C(=O)C_6H_5$

III (a) R = CH_2CH_3
(b) R = H



$C_6H_5C(=O)CH_2CH(CH_2COOH)C(=O)C_6H_5$

IV



$C_6H_5C(=O)CH_2CH(SR)C(=O)C_6H_5$

V (a) R = *n*-C_4H_9
(b) R = *n*-C_5H_{11}

Both *n*-butyl mercaptan and *n*-amyl mercaptan reacted with 1,2-dibenzoylethylene (I) in the presence of piperidine to give addition products (V) in high yield. Attempts to oxidize the products to the corresponding sulfones resulted in degradation back to 1,2-dibenzoylethylene (I). The ease of removal of the addend is indicative that the substance is the result of simple addition and that no unexpected reaction occurred.

EXPERIMENTAL[5]

Sodium bisulfite addition compound (II) *of trans-1,2-dibenzoylethylene* (I). A solution of 30 g. of sodium bisulfite in 50 ml. of water was shaken for 13 hours with a solution of 5 g. of I[6] in 25 ml. of benzene. The precipitated material was filtered and washed with benzene, yielding a mixture of the addition compound and sodium bisulfite melting with decomposition at 240–260°. Separation of the filtrate and evaporation of the benzene layer gave 2.5 g. of unreacted 1,2-dibenzoylethylene (I). Recrystallization of the crude addition product from salt water gave 2.6 g. of material melting with decomposition at 236° (yield based on starting material consumed, 68%); recrystallized from ethyl alcohol, m.p. (dec.) 230–231°. The substance gave a positive sodium fusion test for sulfur. It analyzed correctly for the monohydrate.

Anal. Calc'd for $C_{16}H_{13}NaO_5S\cdot H_2O$: C, 53.62; H,4.22. Found: C, 53.39; H, 4.29.

The material was recovered unchanged after a solution of it in 10% hydrochloric acid was refluxed for 4 hours.

When the preceding reaction was attempted with *trans-1,2-dibenzoylpropene* for about 24 hours no precipitate was formed. Evaporation of the benzene layer gave a 94% recovery of starting material.

Ethyl 2,3-dibenzoyl-1,1-propanedicarboxylate (IIIa). The general procedure of Connor and McClellan was used.[7] A mixture of 5 g. (0.021 mole) of *trans*-1,2-dibenzoylethylene (I), 20 ml. of absolute ethanol, 3.4 g. (0.021 mole) of ethyl malonate, and 0.4 ml. of piperidine was refluxed for 19 hours during which time solution occurred. The reaction mixture then was diluted with 200 ml. of water and extracted with ether. The ether extract was washed and evaporated. The residue was crystallized from isopropyl ether, m.p. 65–66°.

Anal. Calc'd for $C_{23}H_{24}O_6$: C, 69.68; H, 6.10. Found: C, 69.45; H, 6.20.

Attempted preparation of this substance by the interaction of 1-bromo-1,2-dibenzoylethane[8] and sodio diethyl malonate in absolute ethanol solution resulted in dehydrobromination[9] to I in 87% yield; identification by the mixture melting point method.

Attempted Michael condensation with trans-1,2-dibenzoylpropene by the method just described with I gave only a brown intractable oil. Using sodium methoxide as the condensing agent, a 50% recovery of starting material plus an intractable oil was obtained.

2,3-Dibenzoyl-1,1-propanedicarboxylic acid (IIIb). To a hot solution of 1 g. (0.0025 mole) of IIIa and 20 ml. of ethyl

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[1] Taken from a portion of the Ph.D. dissertation of J. C. S., June 1954.

[2] (a) Lutz and Bailey, *J. Am. Chem. Soc.*, **67**, 2229 (1945). (b) Bailey, Nowlin, Pomerantz, Waggoner, and Kawas, *J. Am. Chem. Soc.*, **73**, 5560 (1951). (c) Bailey and Pomerantz, *J. Am. Chem. Soc.*, **75**, 281 (1953). (d) Lutz and McGinn, *J. Am. Chem. Soc.*, **64**, 2585 (1942).

[3] Prepared earlier in crude form by Lutz, Love, and Palmer, *J. Am. Chem. Soc.*, **57**, 1953 (1935).

[4] Gardner and Rydon, *J. Chem. Soc.*, 45 (1938).

[5] All melting points are corrected. Some of the analyses were done by Clark Microanalytical Laboratories, Urbana, Illinois, and some by the Analytical Laboratories of the Biochemical Institute, The University of Texas.

[6] Lutz, in Horning, *Org. Syntheses*, Coll. Vol. **3**, 248 (1955).

[7] Connor and McClellan, *J. Org. Chem.*, **3**, 570 (1939).

[8] Paal and Schulze, *Ber.*, **35**, 168 (1902).

[9] Incidentally, the fact that dehydrohalogenation rather than displacement occurred probably nullifies the proof of structure used by Gardner and Rydon[4] for the product of the Claisen condensation between *trans*-1,2-dibenzoylethylene (I) and ethyl benzylmalonate. They used 1-chloro-1,2-dibenzoylethane and sodio ethyl benzylmalonate. In spite of this, however, there seems little doubt as to the identity of their product.

alcohol was added 5 ml. of 1 *N* sodium hydroxide solution. The resulting solution was refluxed for 2 hours, cooled, and poured into 200 ml. of water. The water solution was washed with ether and then was acidified (to *p*H 2). Extraction with ether, evaporation of the ether extract, and crystallization of the residual oil (by addition of ligroin to a hot isopropyl ether solution of the oil, followed by cooling) gave 0.7 g. (82% yield) of material melting at 132–135°. Recrystallization from a 50–50 isopropyl ether-ligroin mixture raised the melting point to 135–136° (dec.).

Anal. Calc'd for $C_{19}H_{16}O_6$: C, 67.05; H, 4.74; Neut. equiv., 170. Found: C, 67.03; H, 4.81; Neut. equiv., 171.

β,γ-Dibenzoylbutyric acid (IV). A suspension of 1 g. of IIIb in 10 ml. of *n*-hexyl ether was heated at 140–145° until evolution of carbon dioxide ceased and solution occurred. Upon being cooled, the solution deposited 0.87 g. (100% yield) of colorless crystals melting at 143–148°; recrystallized from ethyl alcohol, m.p. 148–150°.

Anal. Calc'd for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44; Neut. equiv., 296. Found: C, 73.29; H, 5.59; Neut. equiv., 298.

2-Butylmercapto-1,2-dibenzoylethane (Va). To a solution of 2.6 g. (0.011 mole) of I in 18 ml. of benzene was added 1 g. (0.011 mole) of *n*-butyl mercaptan and 3 drops of piperidine. Heat was evolved. After 50 minutes the solution was evaporated and the residue was crystallized from ethyl alcohol yielding 3.5 g. (97% yield) of the addition compound melting at 85–88°; recrystallized from ethyl alcohol, m.p. 88–89°. A sodium fusion test for sulfur was positive.

Anal. Calc'd for $C_{20}H_{22}O_2S$: C, 73.58; H, 6.79. Found: C, 73.40; H, 6.92.

2-Amylmercapto-1,2-dibenzoylethane (Vb) was prepared in an identical manner to Va using *n*-amyl mercaptan. Recrystallized from ethyl alcohol, m.p. 94–95°; yield 91%.

Anal. Calc'd for $C_{21}H_{24}O_2S$: C, 74.08; H, 7.11. Found: C, 74.10; H, 7.16.

This substance was also prepared by treatment of 1-bromo-1,2-dibenzoylethane[8] with amyl mercaptan in ethanol solution containing 1 mole of sodium ethoxide per mole of the mercaptan. The mixture was refluxed for 2 hours, evaporated, and the residue was crystallized from ethyl alcohol; 65% yield of Vb melting at 89–91°, identification by the mixture melting point method. Rather than simple displacement, the reaction probably involved dehydrobromination followed by addition of the mercaptan to dibenzoylethylene, since 1-bromo-1,2-dibenzoylethane failed to react with silver amyl mercaptide (from the mercaptan and silver nitrate) after 14 hours of reflux in benzene or in ethanol solution.

Attempted oxidation of Va by treatment with excess 30% hydrogen peroxide reagent in acetone solution for 26 hours at room temperature gave only I in 73% yield, m.p. 108–112°, identification by the mixture melting point method.

Attempted reaction between trans-1,2-dibenzoylpropene and amyl mercaptan by the procedure used for I gave only intractable oils containing from 10–50% unreacted 1,2-dibenzoylpropene, as determined by treatment of the oil with morpholine to give 1,2-dibenzoyl-3-morpholinopropane.[2a] Various basic catalysts (piperidine, sodium methoxide, Triton B), various reaction periods (5 minutes to 13 hours) and various temperatures (room temperature to reflux) were used, all with the same result.

Attempted addition of hydrogen cyanide to trans-1,2-dibenzoylethylene (I) by the general method of Allen and Kimball[10] gave only a red intractable oil. The reaction was not attempted with *trans*-1,2-dibenzoylpropene.

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[10] Allen and Kimball in Blatt, *Org. Syntheses*, **Coll. Vol. 2**, 498 (1943).