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

cis-3-Bromo-1,2-dibenzoylpropene[1]

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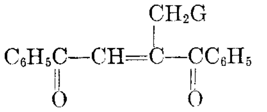
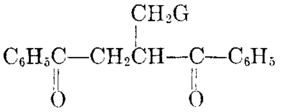
The reactions in the presence of hydrogen, morpholine, alcohol, water, and hydrogen bromide of *cis*-3-bromo-1,2-dibenzoylpropene, which is, at once, an allylic bromide and an unsaturated diketone, are reported. The reactions include addition, cyclization, and displacement.

In earlier papers the displacement and cyclization reactions of *cis*-1,2-dibenzoyl-3-morpholinopropene (Id)[2] and *cis*-2,3-dibenzoyl-2-propen-1-ol (Ic)[3] were described. The present paper deals with the preparation and reactions of the similarly constructed *cis*-3-bromo-1,2-dibenzoylpropene (Ia).

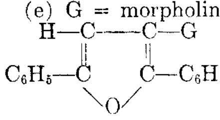
The bromopropene (Ia) was prepared by the characteristic nitric acid oxidation[4] of 3-bromomethyl-2,5-diphenylfuran (IIa), which was obtained in better yield by the bromomethylation of 2,5-diphenylfuran (IIe) than by the addition of hydrogen bromide to 1,2-dibenzoylpropene.[5] It is interesting to note that 2,5-diphenylfuran (IIe) will undergo either mono- or di-bromomethylation[6] in good yield, depending on the relative amount of paraformaldehyde used.


$C_6H_5C(=O)CH{=}C(CH_2G)C(=O)C_6H_5$

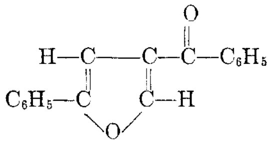
I (a) G = Br (*cis*)
(b) G = H (*cis*)
(c) G = OH (*cis*)
(d) G = morpholino (*cis*)
(e) G = morpholino (*trans*)


$C_6H_5C(=O)CH_2CH(CH_2G)C(=O)C_6H_5$

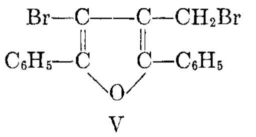
III (a) G = H
(b) G = morpholino



II (a) G = CH_2Br
(b) G = CH_3
(c) G = CHO
(d) G = $CHBr_2$
(e) G = H



IV



V

Reduction of the bromopropene (Ia) by various means led to four different products. Similar to the reduction of *cis*-1,2-dibenzoyl-3-morpholinopropene (Id),[2] an interesting solvent effect was noted. With hydrogen and a platinum catalyst in acetic acid, preferential hydrogenation of the conjugated system of Ia occurred to yield the bromomethylfuran (IIa) (1,6-addition followed by cyclization and loss of water),[7] whereas in ethanol preferential hydrogenolysis of the allylic bromo group occurred to yield *cis*-1,2-dibenzoylpropene (Ib). In each case the reaction was stopped after the absorption of approximately one mole of hydrogen per mole of Ia. Zinc and acetic acid reduction gave a mixture of 3-methyl-2,5-diphenylfuran (IIb) and 1,2-dibenzoylpropane (IIIa). The reaction leading to *cis*-1,2-dibenzoylpropene (Ib) is interesting not only in that it verifies the configuration assigned to Ia on the basis of its preparative method,[4] but also because the stereospecificity requires a simple hydrogenolysis to have occurred rather than the conjugate reaction proposed in the case of the morpholinopropene (Id) which gave 1,2-dibenzoylpropane (IIIa) upon catalytic reduction in ethanol solution.[2]

In earlier papers the easy cyclizations of *cis*-1,2-dibenzoyl-3-morpholinopropene (Id)[2] and *cis*-2,3-dibenzoyl-2-propen-1-ol (Ic)[3] to 4-benzoyl-2-phenylfuran (IV) and 3-formyl-2,5-diphenylfuran (IIc) were noted. *cis*-3-Bromo-1,2-dibenzoylpropene (Ia) behaves similarly. In refluxing absolute ethanol the bromopropene (Ia) is converted to the formylfuran (IIc), whereas in refluxing ethyl alcohol (95%) or a dioxane-water mixture it cyclizes to the benzoylfuran (IV) instead. The presence of bases (potassium hydroxide, sodium ethoxide, or sodium carbonate) causes tar formation.

Since the three compounds in question (Ia, Ic and Id) are similarly constructed it seems likely that the mechanisms of their cyclizations are similar. The cyclization to the formylfuran (IIc) appears to be acid-catalyzed. The morpholinopropene (Id) requires methanolic hydrogen chloride.[2] Although it was reported earlier[3] that the dibenzoylpropenol (Ic) gave the formylfuran (IIc) simply upon treatment with refluxing absolute ethanol, it has since been found that a trace of hydrogen chloride or conc'd sulfuric acid is necessary. With the bromopropene (Ia) it was not necessary to add acid, but undoubtedly some is present through alcoholysis. We believe the mechanism to be similar to the one

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

[2] Bailey and Lutz, *J. Am. Chem. Soc.*, **67**, 2232 (1945).

[3] Bailey, Waggoner, Nowlin, and Rushton, *J. Am. Chem. Soc.*, **76**, 2249 (1954).

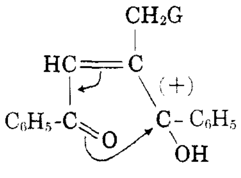
[4] Lutz and Wilder, *J. Am. Chem. Soc.*, **56**, 978 (1934).

[5] Bailey and Pomerantz, *J. Am. Chem. Soc.*, **75**, 281 (1953).

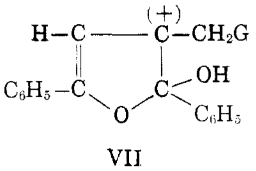
[6] Bailey, Bath, Thomsen, Nelson, and Kawas, J. Org. Chem., **21**, 297 (1956).

[7] Lutz and Reveley, *J. Am. Chem. Soc.*, **61**, 1854 (1939).

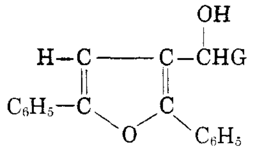
proposed in the morpholinopropene paper[2] with the cyclization being acid-catalyzed (I to VI to VII), followed by loss of a proton and an allylic shift of the hydroxyl group in VII to give VIII, and the loss of water, hydrogen bromide, alcohol or the morpholinium ion in VIII to give IIc. In the case of the bromopropene (Ia) it would be uncertain whether G in VI, VII and VIII would remain Br or be converted to OH or OCH_2CH_3 during the reaction.



VI

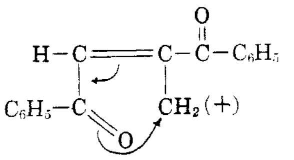


VII



VIII

The cyclizations to the benzoylfuran (IV) probably involve the general mechanism outlined in the morpholinopropene paper,[2] with the exception that in the cases of the bromopropene (Ia) and the propenol (Ic) the solvent probably enters into the reaction to facilitate the removal of the bromide or hydroxyl ion, thus to produce the carbonium ion IX which cyclizes and loses a proton.



IX

Upon treatment with morpholine *cis*-3-bromo-1,2-dibenzoylpropene (Ia) yielded *trans*-1,2-dibenzoyl-3-morpholinopropene (Ie) after 40 minutes, a mixture of Ie and 4-benzoyl-2-phenylfuran (IV) after 24 hours and only IV after 2–3 days. This dependence of the kind of product isolated on the time of the reaction shows that in this particular case, it is not the bromopropene (Ia) which cyclizes to the benzoylfuran (IV), but is the *trans*-morpholinopropene (Ie) instead. The fact that triethylamine failed to bring about the cyclization, but gave a resinous oil instead, also bears this out.

The *trans*-morpholinopropene (Ie) is a new compound. Its reactions are nearly identical with those of the *cis* isomer[2] and establish the structure assigned. Its configuration is assigned on the basis that the previously obtained isomer[2] must have the *cis* configuration because of its preparative method.[4] The fact that the *trans* isomer is produced in a basic medium indicates that it is the stable isomer. No success was obtained, however, in efforts to convert it to the labile *cis* isomer by sunlight. Instead 4-benzoyl-2-phenylfuran (IV) was obtained.

Treatment of *cis*-3-bromo-1,2-dibenzoylpropene with hydrogen bromide in chloroform solution produced 3-dibromomethyl-2,5-diphenylfuran (IId) as the major product and 3-bromo-4-bromomethyl-2,5-diphenylfuran (V) as a minor product. The latter (V) was obtained only after the reaction mixture had stood for 2–3 days, and then the yield was only 13%. The mechanism by which these substances most likely are obtained from the bromopropene (Ia) was proposed in an earlier paper.[5] The reaction leading to IId is another example of the occurrence of 1,3-hydrogen shifts during the reactions of certain 1,2-dibenzoylalkenes and their derivatives.

EXPERIMENTAL[8]

3-Bromomethyl-2,5-diphenylfuran (IIa). To a mixture of 50 g. (0.23 mole) of 2,5-diphenylfuran (Ie) and 450 ml. of glacial acetic acid was added at 10°, 7.5 g. (0.25 mole) of paraformaldehyde and 130 g. (containing 0.48 mole of hydrogen bromide) of 30% hydrogen bromide-acetic acid reagent. The mixture was stirred at 10° for 2 hours during which time the product precipitated; this was filtered off. Additional product was obtained when the filtrate was diluted with water and extracted with ether and the ether extract was washed and partially evaporated. Recrystallization from ligroin gave 45 g. of material melting at 91–93°, recrystallized from ligroin, m.p. 94–95°; identification by conversion to 3-morpholinomethyl-2,5-diphenylfuran hydrochloride (m.p. 218–221°), no depression in a mixture melting point with an authentic sample.[9] From the various filtrates 9 g. of crude product melting at 73–83° was recovered. The total yield was 75%.

cis-3-Bromo-1,2-dibenzoylpropene (Ia). A solution of 36 ml. of conc'd nitric acid, 33 ml. of glacial acetic acid, and 38 ml. of propionic acid was added at 0° to a mixture of 45 g. of 3-bromomethyl-2,5-diphenylfuran (IIa), 150 ml. of propionic acid, and 150 ml. of glacial acetic acid. After 50 minutes the mixture was diluted with one liter of water, extracted with ether, and the ether extract was washed and evaporated to a low volume. Filtration gave 29.5 g. (62%) of material melting at 76–78°, recrystallization from isopropyl ether, m.p. 81–82°.

Anal. Calc'd for $C_{17}H_{13}BrO_2$: C, 62.02; H, 3.98. Found: C, 61.84; H, 4.11.

Reduction of cis-3-bromo-1,2-dibenzoylpropene (Ia). (*a*). *Catalytic in glacial acetic acid.* A solution of 1 g. of the bromopropene (Ia) in 40 ml. of glacial acetic acid was allowed to absorb hydrogen in the presence of Adam's catalyst[10] until approximately one mole of hydrogen per mole of Ia had been absorbed (15–20 minutes) at which time the rate had decreased. The catalyst was removed, the filtrate was diluted with water and extracted with ether, and the ether extract was washed and evaporated, and the residue was recrystallized from isopropyl alcohol, yielding 0.5 g. of material which melted at 91–92° after recrystallization from isopropyl alcohol; no depression in melting point in admixture with known 3-bromomethyl-2,5-diphenylfuran (IIa).

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(8) All melting points are corrected. Some of the analyses were done by the Clark Microanalytical Laboratories, Urbana, Illinois and by the Analytical Laboratory of the Biochemical Institute, The University of Texas.

(9) Lutz and Bailey, *J. Am. Chem. Soc.*, 67, 2229 (1945).

(10) Adams, Voorhees, and Shriner in Gilman and Blatt, *Org. Syntheses*, Coll. Vol. 1, 2nd Ed., 463 (1941).

(*b*). *Catalytic in ethyl alcohol.* A solution of 2 g. of the bromopropene (Ia) in 50 ml. of ethyl alcohol was allowed to absorb hydrogen in the presence of Adam's catalyst[10] until the rate decreased drastically (1.5 moles of H_2 per mole of Ia). The catalyst was removed, and the filtrate was diluted with 250 ml. of 25% calcium chloride solution and extracted with ether. The ether layer was washed and evaporated and the residue was crystallized from isopropyl ether, giving 0.65 g. of *cis*-1,2-dibenzoylpropene (Ib) melting at 60–62° after recrystallization from isopropyl ether; identification by a mixture melting point with an authentic sample.[11]

(*c*). *Reduction with zinc and acetic acid.* To a solution of 3 g. of the bromopropene (Ia) in 75 ml. of glacial acetic acid was added excess zinc dust. After about 5 minutes the unreacted zinc was removed. The filtrate was diluted with water and extracted with ether, the ether extract was washed and evaporated, and the residue was recrystallized from ethyl alcohol, yielding 1.8 g. of material melting at 45–75°. Recrystallization from 20 ml. of isopropyl ether gave 0.62 g. (27%) of material melting at 95–99° which was shown to be 1,2-dibenzoylpropane (IIIa) by a mixture melting point with an authentic sample (m.p. 102–103°).[12] Evaporation of the filtrate and crystallization of the residue from ethyl alcohol (Darco) gave 0.61 g. (29%) of material melting at 52–55° which showed no depression in a mixture melting point with known 3-methyl-2,5-diphenylfuran (IIb).[11]

Cyclization of cis-3-bromo-1,2-dibenzoylpropene (Ia) *to 3-formyl-2,5-diphenylfuran* (IIc). A solution of 1 g. of Ia and 50 ml. of commercial absolute ethanol was refluxed for 2 hours and then was allowed to stand overnight. The solution then was diluted with water and extracted with ether, the ether extract was evaporated, and the residue was crystallized from ethyl alcohol, yielding 0.55 g. (73%) of 3-formyl-2,5-diphenylfuran melting at 86–89°; recrystallized from ethyl alcohol, m.p. 88–90°, identification by a mixture melting point with an authentic sample.[2] The results were the same with absolute ethanol distilled from sodium ethoxide, except that the yield was only 20%.

Cyclization of cis-3-bromo-1,2-dibenzoylpropene (Ia) *to 4-benzoyl-2-phenylfuran* (IV). A solution of 1 g. of the bromopropene (Ia), 20 ml. of dioxane, and 10 ml. of water was refluxed for 20 hours, after which time the hot solution was diluted with water. On cooling, a mixture of an oil and a crystalline solid precipitated. On standing, the oil crystallized. Filtration yielded 0.6 g. (80%) of material melting at 104–109°; recrystallized from carbon tetrachloride, m.p. 111–114°, no depression in a mixture melting point with known 4-benzoyl-2-phenylfuran (IV).[13] With a reflux period of only 2 hours an 85% recovery of Ia was obtained.

A solution of 1 g. of Ia and 50 ml. of 95% ethyl alcohol refluxed for 10 hours gave a 52% yield of IV (m.p. 109–112°). After only a 2 hour reflux period an 85% recovery of Ia was obtained.

Attempted hydrolyses and alcoholyses of 3-bromo-1,2-dibenzoylpropene (Ia) with such reagents as potassium hydroxide in ethyl alcohol, sodium carbonate in 80% ethyl alcohol, and sodium ethoxide in absolute ethanol led to tar formation in all cases.

Reaction of cis-3-bromo-1,2-dibenzoylpropene (Ia) with hydrogen bromide. (*a*). *To give 3-dibromomethyl-2,5-diphenylfuran* (IId). To 100 ml. of a chloroform solution containing 0.5 g. (0.006 mole) of hydrogen bromide was added 2 g. (0.006 mole) of the bromopropene (Ia) and the resulting solution was allowed to stand for 25 hours. It then was washed and evaporated and the residue was crystallized from ligroin, yielding 1.2 g. (50%) of material melting at 120–126°. Recrystallization from ligroin raised the melting point to 126–129°; the material showed no melting point depression in admixture with an authentic sample of 3-dibromomethyl-2,5-diphenylfuran (IId).[6] Using either 1 mole or 2 moles of hydrogen bromide per mole of Ia in chloroform solution for only 30 minutes, the yield of IId was 30%. No other crystalline materials could be isolated.

(*b*). *To give 3-bromo-4-bromomethyl-2,5-diphenylfuran* (V). A solution of 2 g. (0.006 mole) of Ia, 1.0 g. (0.012 mole) of hydrogen bromide, and 100 ml. of chloroform was allowed to stand for 52 hours after which time it was washed and evaporated and the residue was crystallized from ligroin (1.6 g., m.p. 65–74°). Fractional recrystallization from isopropyl alcohol gave 0.3 g. (13%) of material melting at 88–91° which showed no depression in a mixture melting point with known 3-bromo-4-bromomethyl-2,5-diphenylfuran (V).[5]

Reaction of cis-3-bromo-1,2-dibenzoylpropene (Ia) *in the presence of morpholine.* (*a*). *To give 4-benzoyl-2-phenylfuran* (IV). To a solution of 0.7 g. (0.002 mole) of the bromopropene (Ia) in 25 ml. of ether was added 2 g. (0.023 mole) of morpholine. A white precipitate immediately formed (morpholine hydrobromide). After about 60 hours the mixture was thoroughly washed and then evaporated. Recrystallization of the crystalline residue from ethyl alcohol gave 0.5 g. of 4-benzoyl-2-phenylfuran melting at 110–113°; identification by the mixture melting point method.

(*b*). *To give trans-3-morpholino-1,2-dibenzoylpropene* (Ie). A solution of 8.7 g. (0.026 mole) of the bromopropene (Ia), 17 g. (0.2 mole) of morpholine and 240 ml. of ether was allowed to stand for 40 minutes after which time it was washed thoroughly with water and extracted with 250 ml. of about 3 *N* hydrochloric acid. Evaporation of the ether layer gave as the neutral product only a small amount of a yellow oil. The hydrochloric acid layer was neutralized with sodium carbonate and extracted with 250 ml. of ether. Upon evaporation of the ether extract to about 100 ml., 4.4 g. of yellow crystals melting at 105–114° was filtered off. Evaporation to dryness gave an additional 2.7 g., m.p. 92–99°; total yield 81%. Several recrystallizations from isopropyl ether raised the melting point to 118–119°. The material was shown to be different from the colorless *cis* isomer (Id) by a mixture melting point with an authentic sample (m.p. 126–128°).[9]

Anal. Calc'd for $C_{21}H_{21}NO_3$: C, 75.20; H, 6.31; N, 4.18. Found: C, 75.56; H, 6.22; N, 4.21.

Using one mole of morpholine per mole of Ia for 24 hours and working up the reaction mixture in the same manner there was obtained a 40% yield of the benzoylfuran (IV) as the neutral product and a 44% yield of the morpholinopropene (Ie) as the basic product. With 2 moles of morpholine per mole of Ia for 24 hours a 62% yield of the morpholinopropene (Ie) was obtained and with about 8 moles of morpholine per mole of Ia for 24 hours the yield of IV was 54% and, of Ie, 24%. The *trans* morpholinopropene (Ie) is stable to acetic acid-nitric acid mixtures at room temperature. These are the conditions under which the *cis*-isomer is prepared.[9]

Reaction of cis-3-bromo-1,2-dibenzoylpropene (Ia) *in the presence of triethylamine* (2 moles per mole of Ia) in ether solution gave no precipitate of triethylamine hydrobromide. After 10 hours the reaction mixture was worked up in the same manner as in the morpholine experiments. No basic product was obtained and only an intractable oil was obtained as the neutral product.

Reduction of trans-1,2-dibenzoyl-3-morpholinopropene (Ie) *with zinc and acetic acid* by the procedure used earlier for the *cis* isomer (Id)[9] gave a 75% yield of 1,2-dibenzoyl-3-morpholinopropane (IIIb), m.p. 82–85°, identification by a mixture melting point with an authentic sample.[9]

Catalytic reduction of trans-1,2-dibenzoyl-3-morpholinopropene (Ie) *in ethyl alcohol.* A solution of 1 g. (0.003 mole) of Ie in 100 ml. of ethyl alcohol was allowed to absorb hydrogen in the presence of Adam's catalyst[10] until the rate

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(11) Lutz and McGinn, *J. Am. Chem. Soc.*, **64**, 2585 (1942).

(12) Lutz and Taylor, *J. Am. Chem. Soc.*, **55**, 1168 (1933).

(13) Fuson, Fleming, and Johnson, *J. Am. Chem. Soc.*, **60**, 1994 (1938).

sharply decreased, at which time 0.006 mole had been absorbed. The catalyst was removed, the filtrate was evaporated, and the residue was treated with 50 ml. of ether and 25 ml. of 1 *N* hydrochloric acid. The ether layer yielded 0.64 g. (85%) of 1,2-dibenzoylpropane (IIIa) which melted at 102–104° after recrystallization from ethyl alcohol and was identified by a mixture melting point with an authentic sample.[12] From the aqueous layer, after neutralization with sodium carbonate, extraction with ether, evaporation of the ether extract, and crystallization of the residue from ethyl alcohol, was obtained 0.14 g. (14% yield) of 1,2-dibenzoyl-3-morpholinopropane (IIIb), m.p. 82–84°, identification by a mixture melting point with an authentic sample.[9]

Treatment of trans-1,2-dibenzoyl-3-morpholinopropene (Ie) *with methanolic hydrogen chloride* in the same manner as reported earlier[2] for the *cis* isomer (Id) gave a 68% yield of 3-formyl-2,5-diphenylfuran (IIc) and a 30% recovery of starting material (from the water washings). The formylfuran (IIc) melted at 88–91° and showed no melting point depression in admixture with an authentic sample.[2]

On exposure to sunlight (benzene solution) trans-1,2-dibenzoyl-3-morpholinopropene (Ie) was converted after 6 hours to 4-benzoyl-2-phenylfuran (IV) in 41% yield, m.p. 106–110°, identification by a mixture melting point with an authentic sample.[13] In the work-up procedure, the benzene solution was extracted with dilute hydrochloric acid and evaporated, and the residue was crystallized from ethyl alcohol. From the acid layer was obtained an inseparable mixture (1 g.) melting at 103–113°. The *cis*-morpholinopropene (Id) behaved similarly upon exposure to sunlight.

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