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

Further Studies Concerning the Reactions of Halogens with 1,2-Dibenzoylpropene[1]

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The reaction of 1,2-dibenzoylpropene with bromine is shown to involve a complicated set of equilibria. In ether solution the product is 1,2-dibenzoyl-1,2-dibromopropane. This very unstable substance appears to be the precursor to 3-bromo-4-(bromomethyl)-2,5-diphenylfuran and possibly to 3-(dibromomethyl)-2,5-diphenylfuran, products of the reaction between bromine and 1,2-dibenzoylpropene in chloroform solution. The reaction between chlorine and 1,2-dibenzoylpropene normally does not go past the 1,2-dibenzoyl-1,2-dichloropropane stage.

In an earlier paper[2] it was reported that *trans*-1,2-dibenzoylpropene (III) reacts with bromine in chloroform solution to produce 3-(dibromomethyl)-2,5-diphenylfuran (X) and 3-bromo-4-(bromomethyl)-2,5-diphenylfuran (XII). The latter substance (XII) was isolated only in experiments which were worked up shortly after the bromine color disappeared (about 45 minutes). After reaction periods of 24 hours only the (dibromomethyl)furan (X) could be isolated. It was proposed[2] that the intermediate in the formation of these two substances (X and XII) was the then unknown 3-bromo-1,2-dibenzoylpropene (VI), obtained through a substitution reaction with 1,2-dibenzoylpropene (III). The present paper deals with a further study of the reactions of halogens with 1,2-dibenzoylpropene (III).

Since the work just described, *cis*-3-bromo-1,2-dibenzoylpropene (VI) has been synthesized and has been found to react with hydrogen bromide in chloroform solution to give either 3-(dibromomethyl)-2,5-diphenylfuran (X) or 3-bromo-4-(bromomethyl)-2,5-diphenylfuran (XII).[3] The latter substance (XII), however, was isolated in very low yield and only after the reaction mixture had stood for 52 hours. On the other hand, it was possible to isolate the (dibromomethyl)furan (X) after only 30 minutes. The isolation of X early in the reaction and of XII only after many hours is just the opposite of the results found in the reaction of bromine with 1,2-dibenzoylpropene (III) and shows that the reaction is more complicated than first proposed.[2]

When the reaction between 1,2-dibenzoylpropene (III) and bromine was carried out in ether solution for 28 hours, a mixture was obtained from which was isolated 3-(dibromomethyl)-2,5-diphenylfuran (X). When the reaction mixture was worked up as soon as the bromine color disappeared (3–5 minutes), however, an unstable compound identified as the addition product, 1,2-dibenzoyl-1,2-dibromopropane (IV), was obtained. This substance slowly evolves hydrogen bromide at room temperature. It was identified through dehydrohalogenation to *cis*-1-bromo-1,2-dibenzoylpropene (VIII) upon treatment with alcoholic potassium hydroxide.

Upon treatment of either the addition compound (IV) or its dehydrohalogenation product (VIII) with hydrogen bromide in chloroform solution, 3-bromo-4-(bromomethyl)-2,5-diphenylfuran (XII) was obtained in good yield. Conversion to 3-(dibromomethyl)-2,5-diphenylfuran (X) was accomplished, however, only with the addition compound (IV).

The facts just presented require the conclusion that in the interaction between 1,2-dibenzoylpropene (III) and bromine in chloroform solution[2] many reactions, most or all of which are equilibrium reactions, are taking place at once, as shown in the accompanying diagram. In agreement with this conclusion is the fact that in the bromine reaction, the yield of neither 3-(dibromomethyl)-2,5-diphenylfuran (X) nor 3-bromo-4-bromomethyl-2,5-diphenylfuran (XII) was ever over 50%.

To the present authors the best interpretation of these data is that 3-bromo-4-bromomethyl-2,5-diphenylfuran (XII) originates in the bromine plus 1,2-dibenzoylpropene (III) reaction in chloroform solution predominantly through the equilibria involving structures III, IV, VIII, VII, XI, and XII. The path leading to 3-(dibromomethyl)-2,5-diphenylfuran (X) isn't quite so clear. The facts that no success was attained in efforts to convert VIII to X and that IV was converted to X in rather poor yield would seem to speak against the route involving compounds IV, VIII, VII (or IV directly to VII), VI, V, IX, and X. However, it should be noted that in the actual reaction between 1,2-dibenzoylpropene (III) and bromine, the intermediate IV probably loses hydrogen bromide only slowly and the concentration of hydrogen bromide in the reaction mixture is probably never large. On the other hand, in the reactions between IV or VIII and hydrogen bromide, excess hydrogen bromide was always present. Thus, it could be possible that during the course of the reactions starting with IV or VIII, compound XI was cyclized, by the acidic conditions,

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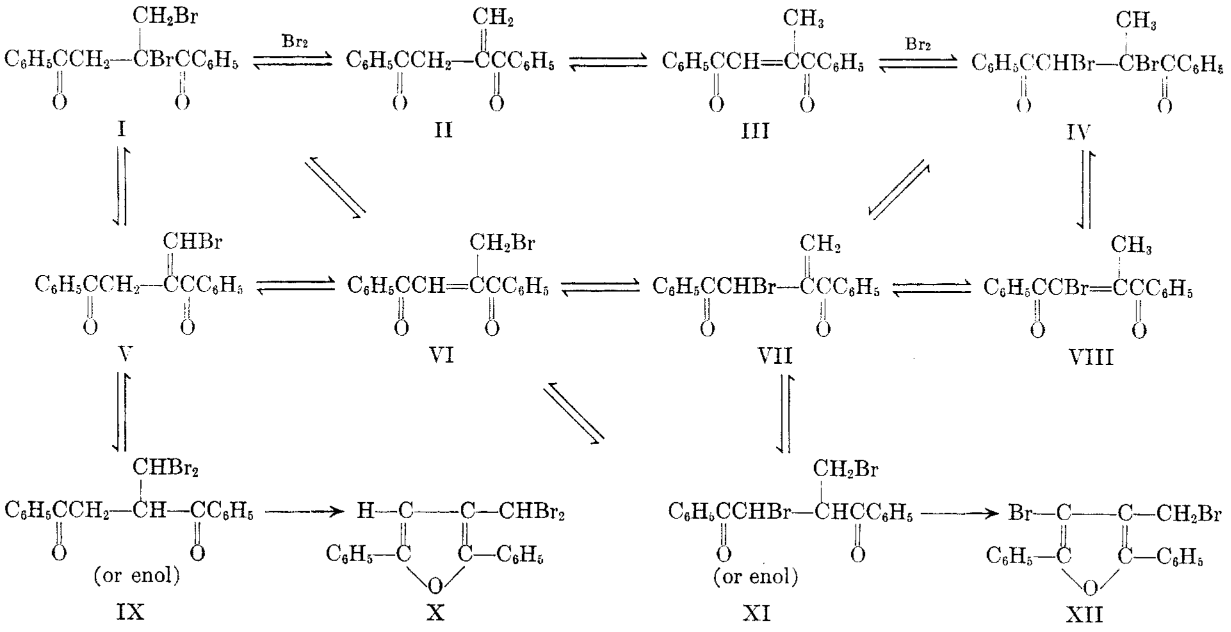
(1) Taken from portions of the Ph.D. dissertation of J. C. S., June, 1954, and the M.A. thesis of C. F. F., August, 1955.

(2) Bailey and Pomerantz, *J. Am. Chem. Soc.*, **75**, 281 (1953).

(3) Bailey and Smith, *J. Org. Chem.*, **21**, 628 (1956).



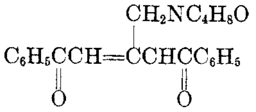
to 3-bromo-4-(bromomethyl)-2,5-diphenylfuran (XII) before the equilibria leading to 3-(dibromomethyl)-2,5-diphenylfuran (X) could be established. Thus the route just suggested is not necessarily eliminated. Neither, however, is the alternate route involving structures III, II, I, VI, V (or I directly to V), IX, and X. The originally suggested substitution reaction of 1,2-dibenzoylpropene (III) leading directly to 3-bromo-1,2-dibenzoylpropene (VI) seems to be eliminated, however, by the fact that this should lead to 3-(dibromomethyl)-2,5-diphenylfuran (X) early in the reaction (note experiment starting with VI) rather than late in the reaction as actually found.

It is to be noted that throughout the equilibria just discussed the 1,3-hydrogen shift, found to be characteristic of 1,2-dibenzoylpropene (III) and similar compounds,[2,4] plays a prominent role.

The reaction between 1,2-dibenzoylpropene (III) and chlorine does not normally proceed as far as the reaction with bromine. In carbon tetrachloride 1,2-dibenzoyl-1,2-dichloropropane was the product in good yield. It was much more stable than its analog (IV), and this probably accounts for the fact that the chlorine reaction stops at this point.

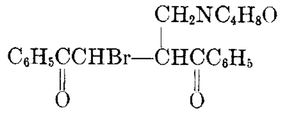
Like the dibromopropane (IV), 1,2-dibenzoyl-1,2-dichloropropane is dehydrohalogenated by alcoholic potassium hydroxide to *cis*-1-chloro-1,2-dibenzoylpropene (analog of VIII). Both the addition compound and its dehydrochlorination product react with excess hydrogen chloride in chloroform solution to give 3-chloro-4-(chloromethyl)-2,5-diphenylfuran (analog of XII). No 3-(dichloromethyl)-2,5-diphenylfuran (analog of X) was found in the reaction mixture.

Both 1,2-dibenzoyl-1,2-dichloropropane and its dibromo analog (IV) react with morpholine to give 1-chloro-1,2-dibenzoylpropene and its bromo analog (VIII), respectively, plus a low yield of *trans*-1,2-dibenzoyl-3-morpholinopropene (XIII). In order to determine the mode of formation of XIII, both 1-chloro-1,2-dibenzoylpropene and its bromo analog (VIII) were treated with morpholine. They were likewise found to be converted in low yield to *trans*-1,2-dibenzoyl-3-morpholinopropene (XIII). It is apparent then, illustrating with the bromo analogs, that the reactions proceed through the equilibrium between VIII and VII, followed either by an allylic displacement reaction upon VII, involving rearrangement, or else by an addition of morpholine to VII (to give XIV) followed by dehydrohalogenation.



$$\mathrm{C_6H_5\underset{\substack{\Vert\\O}}{C}CH{=}\overset{\substack{CH_2NC_4H_8O\\|}}{C}CH\underset{\substack{\Vert\\O}}{C}C_6H_5}$$

XIII



$$\mathrm{C_6H_5\underset{\substack{\Vert\\O}}{C}CHBr{-}\overset{\substack{CH_2NC_4H_8O\\|}}{C}H\underset{\substack{\Vert\\O}}{C}C_6H_5}$$

XIV

It is interesting to note that the dehydrohalogenation of 1,2-dibenzoyl-1,2-dibromopropane (IV) and its dichloro analog to the corresponding *cis*-1,2-dibenzoyl-1-halopropenes (VIII and its chloro analog) under alkaline conditions constitutes chemical evidence to corroborate the spectral evidence of Kuhn, Lutz, and Bauer[5] that the *cis*-1,2-dibenzoyl-1-halopropenes are the more stable of the *cis* and *trans* isomers.

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(4) (a) Lutz and Bailey, *J. Am. Chem. Soc.*, **67**, 2229 (1945). (b) Bailey and Nowlin, *J. Am. Chem. Soc.*, **71**, 732 (1949). (c) Bailey and Hakki, *J. Am. Chem. Soc.*, **71**, 2886 (1949). (d) Bailey, Nowlin, Pomerantz, Waggoner, and Kawas, *J. Am. Chem. Soc.*, **73**, 5560 (1951). (e) Bailey, Bath, Thomsen, Nelson, and Kawas, *J. Org. Chem.*, **21**, 297 (1956).

(5) Kuhn, Lutz, and Bauer, *J. Am. Chem. Soc.*, **72**, 5058 (1950).

EXPERIMENTAL[6]

Reaction of bromine with trans-1,2-dibenzoylpropene (III) *in ether.* (*a*). *To give 1,2-dibenzoyl-1,2-dibromopropane* (IV). To a solution of 15 g. (0.06 mole) of *trans*-1,2-dibenzoylpropene (III) in 250 ml. of absolute ether was added 9.6 g. (0.06 mole) of bromine. After 3 minutes the bromine color had disappeared. Fumes of hydrogen bromide were slowly evolved. Upon partial evaporation of the solution, crystallization occurred giving 12.7 g. (52% yield) of material melting sharply with decomposition somewhere between 84° and 88°. The material slowly evolved hydrogen bromide on standing. All attempts to recrystallize it caused its decomposition. It was immediately analyzed for removable bromide ion by titration with standard sodium hydroxide solution.

Anal. Calc'd for $C_{17}H_{14}Br_2O_2$: $Br^{(-)}$, 19.49; Found: $Br^{(-)}$, 20.26.

(*b*). *To give 3-(dibromomethyl)-2,5-diphenylfuran* (X). A solution of 2 g. (0.008 mole) of III, 1.3 g. (0.008 mole) of bromine, and 100 ml. of absolute ether was allowed to stand for 28 hours, after which time it was evaporated. Crystallization of the residue from isopropyl alcohol gave 1.3 g. (42% yield) of 3-(dibromomethyl)-2,5-diphenylfuran (X) melting at 118–124°; recrystallized from isopropyl alcohol, m.p. 126–129°; identification by a mixture melting point with an authentic sample.[2]

1,2-Dibenzoyl-1,2-dichloropropane. To a solution of 2 g. (0.008 mole) of *trans*-1,2-dibenzoylpropene (III) in 50 ml. of carbon tetrachloride was added 9 ml. of a 0.9 *M* chlorine-carbon tetrachloride solution (containing 0.008 mole, prepared by saturating carbon tetrachloride with chlorine and standardized by treating with KI and titrating with 0.1 *N* $Na_2S_2O_3$). After standing for 3 hours in a stoppered flask, the solution was evaporated and the residue was crystallized from methanol giving 1.8 g. (70% yield) of material melting at 97–100°; recrystallized from methanol, m.p. 101–102°. The substance gave positive Beilstein and silver nitrate tests for halogen.

Anal. Calc'd for $C_{17}H_{14}Cl_2O_2$: C, 63.57; H, 4.39. Found: C, 63.34; H, 4.41.

The yield of the addition compound was similar after a reaction period of 19 hours. Reaction periods of less than 3 hours resulted in lowered yield or no reaction. In chloroform solution only intractable oils were obtained.

cis-1-Chloro-1,2-dibenzoylpropene. (*a*). *From 1,2-dibenzoyl-1,2-dichloropropane.* To a boiling solution of 2.7 g. (0.0084 mole) of 1,2-dibenzoyl-1,2-dichloropropane in 100 ml. of ethyl alcohol was added 0.5 g. (0.009 mole) of potassium hydroxide in 20 ml. of ethyl alcohol. The solution turned red and a precipitate appeared. After one-half hour of reflux the mixture was filtered and the filtrate was diluted with 100 ml. of water and extracted with ether. The ether extract was washed with saturated calcium chloride solution and evaporated. Crystallization of the residue from ethyl alcohol gave 2.1 g. (87% yield) of material melting at 68–70°; recrystallized from ethyl alcohol, m.p. 83–84°.

Anal. Calc'd for $C_{17}H_{13}ClO_2$: C, 71.71; H, 4.60. Found: C, 71.68, 71.20; H, 5.01, 4.57.

(*b*). *From 3-chloro-4-methyl-2,5-diphenylfuran.* 3-Chloro-4-methyl-2,5-diphenylfuran, prepared by the method of Bailey and Pomerantz,[2] was oxidized at room temperature by the general and characteristic method of Lutz and Wilder.[7] The yield of *cis*-1-chloro-1,2-dibenzoylpropene melting at 83–84° was 61%. The substance was shown by a mixture melting point to be identical with the substance obtained by the dehydrohalogenation of 1,2-dibenzoyl-1,2-dichloropropane.

cis-1-Bromo-1,2-dibenzoylpropene (VIII) was obtained from 1,2-dibenzoyl-1,2-dibromopropane (IV) in like manner and yield as was *cis*-1-chloro-1,2-dibenzoylpropene obtained from 1,2-dibenzoyl-1,2-dichloropropane. The material (m.p. 84–86°) was identified by a mixture melting point with an authentic sample.[8]

Reaction of 1,2-dibenzoyl-1,2-dichloropropane with morpholine. To a solution of 4 g. (0.012 mole) of 1,2-dibenzoyl-1,2-dichloropropane in 80 ml. of dry ether was added 6 g. (0.07 mole) of morpholine. A white precipitate formed. After 30 minutes the mixture was diluted with 100 ml. of water and the resulting mixture was extracted with ether. The ether layer was extracted with dilute hydrochloric acid and then was evaporated. Crystallization of the residue from ethyl alcohol gave 3.1 g. (87% yield) of *cis*-1-chloro-1,2-dibenzoylpropene, m.p. 84–85°, identification by the mixture melting point method. Neutralization of the acid extract with sodium carbonate gave 0.7 g. (16% yield) of yellow crystals melting at 108–110°; recrystallized from ethyl alcohol, m.p. 111–113°; identified as *trans*-1,2-dibenzoyl-3-morpholinopropene (XIII) by a mixture melting point with an authentic sample.[3]

When *1,2-dibenzoyl-1,2-dibromopropane* (IV) was treated with morpholine in a similar manner, similar yields of *cis*-1-bromo-1,2-dibenzoylpropene (VIII) and *trans*-1,2-dibenzoyl-3-morpholinopropene (XIII) were obtained.

Reaction of cis-1-bromo-1,2-dibenzoylpropene (VIII) *with morpholine* in a manner similar to that described in the preceding experiment with 1,2-dibenzoyl-1,2-dichloropropane gave a 56% recovery of starting material and a 50% yield (based on starting material consumed) of *trans*-1,2-dibenzoyl-3-morpholinopropene (XIII). Similar results were obtained using *cis-1-chloro-1,2-dibenzoylpropene.*

Reactions of 1,2-dibenzoyl-1,2-dibromopropane (IV) *in the presence of hydrogen bromide.* (*a*). *To give 3-bromo-4-(bromomethyl)-2,5-diphenylfuran* (XII). One gram (0.004 mole) of 1,2-dibenzoylpropene (III) was converted to 1,2-dibenzoyl-1,2-dibromopropane (IV) by the procedure described earlier. After evaporation of the ether solvent, the crude IV was treated with 40 ml. of a solution of hydrogen bromide (0.004 mole) in chloroform and the resulting solution was allowed to stand in a stoppered flask for 70 hours. Evaporation of the reaction mixture gave 0.76 g. (49% yield) of 3-bromo-4-(bromomethyl)-2,5-diphenylfuran (XII) melting at 85–87°; recrystallized from isopropyl alcohol, m.p. 91–92°; identification by a mixture melting point with an authentic sample.[2]

When the same reaction was carried out for 18 hours, the yield of XII was 32%. After 3 hours only an intractable oil was obtained.

(*b*). *To give 3-(dibromomethyl)-2,5-diphenylfuran* (X). Crude 1,2-dibenzoyl-1,2-dibromopropane (IV), prepared as described earlier from 2 g. (0.008 mole) of 1,2-dibenzoylpropene (III), was dissolved in 40 ml. of chloroform, one drop of bromine was added, and dry hydrogen bromide was passed in for 2 minutes. After the resulting solution had stood for 26 hours, it was evaporated. The residue was crystallized from isopropyl alcohol, yielding 0.6 g. (19% yield) of 3-(dibromomethyl)-2,5-diphenylfuran (X) melting at 117–123°; recrystallized from isopropyl alcohol, m.p. 126–128°; identification by the mixture melting point method.

3-Chloro-4-(chloromethyl)-2,5-diphenylfuran. Into a solution of 1 g. (0.003 mole) of 1,2-dibenzoyl-1,2-dichloropropane in 30 ml. of chloroform was passed dry hydrogen chloride for 8 hours. Evaporation of the solution and several

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(6) All melting points are corrected. Some of the microanalyses were done by the Analytical Laboratory of the Biochemical Institute of The University of Texas and by the Weiler and Strauss Microanalytical Laboratory of Oxford, England.

(7) Lutz and Wilder, *J. Am. Chem. Soc.*, **56**, 1193 (1934).

(8) Lutz and Stuart, *J. Am. Chem. Soc.*, **59**, 2316 (1937).

recrystallizations of the residue from isopropyl alcohol gave 0.8 g. (85% yield) of material melting at 74–75°.[9]

Anal. Calc'd for $C_{17}H_{12}Cl_2O$: C, 67.34; H, 3.99; Cl, 23.39. Found: C, 67.37; H, 4.56; Cl, 23.34.

In a similar fashion *cis*-1-chloro-1,2-dibenzoylpropene was converted to 3-chloro-4-(chloromethyl)-furan in 78% yield. Only starting material was recovered, however, if the chloropropene is simply dissolved in a previously prepared solution of hydrogen chloride in chloroform.

Reaction of cis-1-bromo-1,2-dibenzoylpropene (VIII) *with hydrogen bromide.* Two g. (0.006 mole) of *cis*-1-bromo-1,2-dibenzoylpropene (VIII) was dissolved in 25 ml. of a standard chloroform-hydrogen bromide solution containing 0.006 mole of hydrogen bromide. After the solution had stood for 24 hours it was worked up in the same manner as was the corresponding reaction with 1,2-dibenzoyl-1,2-dibromopropane (IV). Thus was obtained 1.3 g. (55% yield) of 3-bromo-4-bromomethyl-2,5-diphenylfuran (XII) which melted at 88–91° after recrystallization from isopropyl alcohol; identification by the mixture melting point method. Using 3 moles of hydrogen bromide to 1 mole of VIII for 44 hours, a 72% yield of XII was obtained. Using mole per mole and a reaction time of 3 hours only an intractable oil was obtained. In no case was any 3-(dibromomethyl)-2,5-diphenylfuran (X) ever isolated, even when the exact conditions which afforded X from 1,2-dibenzoyl-1,2-dibromopropane were repeated.

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(9) This material has been shown to be 3-chloro-4-(chloromethyl)-2,5-diphenylfuran by S. S. Bath who synthesized it by the chloromethylation of 3-chloro-2,5-diphenylfuran. This will be reported in detail in a later paper.