

Hinsberg<sup>14</sup> (two runs), and following the general directions of Reinhalt<sup>15</sup> (one run) and of Hunter<sup>16</sup> (one run) were unsuccessful.

***o,o'*-Dicarboxydiphenyl Sulfoxide.** By Peroxide Oxidation.—A mixture of 1.4 g. (0.005 mole) of *o,o'*-dicarboxydiphenyl sulfide and 25 ml. of ethanol was refluxed on a steam-bath until solution was complete. To the hot solution was added 2 ml. of 30% aqueous hydrogen peroxide. After refluxing for 3.0 hours an additional 1 ml. of peroxide was added and refluxing was continued for 3.0 hours more. An equal volume of hot water was added slowly to the hot solution and heating was discontinued. Filtration of the cooled mixture gave 1.0 g. (71.4%) of pure *o,o'*-dicarboxydiphenyl sulfoxide melting at 310–311°.

**By Permanganate Oxidation.**—The following procedure is essentially that used by Mayer<sup>13</sup> for the reported preparation of *o,o'*-dicarboxydiphenyl sulfone except that the solution was left slightly basic and only a slight excess of permanganate was used. One gram (0.0036 mole) of *o,o'*-dicarboxydiphenyl sulfide was dissolved in a very slight excess of 2% sodium hydroxide and the resulting solution was diluted to 50 ml. with water. A warm solution of 0.8 g. (0.005 mole) of potassium permanganate in 100 ml. of water was added and the resulting solution was warmed overnight on a steam-bath. The precipitated manganese dioxide was filtered off to leave a clear, colorless solution. The filtrate was acidified with a solution of sodium bisulfite to which had been added excess 6 *N* hydrochloric acid. No solid product was obtained until the volume of the solution was reduced to about 25 ml. Filtration gave 0.8 g. of brown flakes which melted at 215–229°. Repeated recrystallizations from glacial acetic acid diluted with xylene resulted in a total yield of pure *o,o'*-dicarboxydiphenyl sulfoxide of 38.1%, m.p. 312–313°. An extensive search of the various filtrates did not reveal the presence of any other compound.

***o,o'*-Dicarboxydiphenyl Sulfone.** By Peroxide Oxidation of *o,o'*-Dicarboxydiphenyl Sulfide.—A mixture of about 1.0 g. of *o,o'*-dicarboxydiphenyl sulfide and 15 ml. of glacial acetic acid was refluxed to give complete solution of the sulfide. To the slightly cooled solution was added 3 ml. of 30% aqueous hydrogen peroxide. After refluxing for 30 min., an additional 1.0 ml. of peroxide was added, refluxing was continued for 30 min. longer, and the solution was allowed to stand overnight at room temperature. No prod-

uct was obtained until the volume of the solution had been reduced to about 1 ml. The crystals were dissolved in 5 ml. of glacial acetic acid and the resulting solution was digested with Norit, filtered hot and cooled. Filtration yielded 0.3 g. of small rectangular plates which melted at 220–221°.

**By Permanganate Oxidation of *o,o'*-Dicarboxydiphenyl Sulfide.**—The following procedure is essentially that reported by Mayer.<sup>13</sup> One gram (0.0036 mole) of *o,o'*-dicarboxydiphenyl sulfide was dissolved in a very slight excess of 2% sodium hydroxide and the solution was back-titrated with 3 *N* hydrochloric acid until the precipitated acid just redissolved. A warm solution of 0.9 g. (0.006 mole) of potassium permanganate in 100 ml. of water was added and the resulting solution was warmed overnight on a steam-bath. The precipitated manganese dioxide was filtered off giving a clear permanganate colored filtrate. A solution of sodium bisulfite which had been made strongly acid with 6 *N* hydrochloric acid was added until the filtrate was colorless and acid in reaction. The solution was evaporated to a volume of about 25 ml., filtered hot and cooled in air. Filtration yielded 0.7 g. (63.6%) of impure material melting at 216–219°. One recrystallization from glacial acetic acid diluted with an equal volume of xylene gave 0.4 g. (36.4%) of pure *o,o'*-dicarboxydiphenyl sulfone melting sharply at 220–221°. A check run following this same procedure gave essentially identical results.

**By Peroxide Oxidation of *o,o'*-Dicarboxydiphenyl Sulfoxide.**—To a solution of about 0.1 g. of *o,o'*-dicarboxydiphenyl sulfoxide in 5 ml. of glacial acetic acid was added 1 ml. of 30% aqueous hydrogen peroxide. After standing for 48 hours the solvent was removed under a water-pump vacuum by distillation from a steam-bath. The residue was recrystallized from glacial acetic acid diluted with an equal volume of xylene to give nearly 0.1 g. of product melting at 212–215°. Two recrystallizations from the same solvent pair raised the melting point to 220–221°. A mixed melting point with the sulfone prepared by permanganate oxidation showed no depression.

In view of the above evidence, the melting point of 137° reported for *o,o'*-dicarboxydiphenyl sulfone by Mayer<sup>13</sup> is believed to be in error. As described above, the sulfone was prepared by peroxide and permanganate oxidation of the corresponding sulfide, by peroxide oxidation of the corresponding sulfoxide and by metalation of diphenyl sulfone with subsequent carbonation, and in all cases the compound melted at 220–221°.

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(14) O. Hinsberg, *ibid.*, **43**, 1877 (1910).

(15) F. E. Reinhalt, *J. Franklin Inst.*, **249**, 248 (1950).

(16) B. A. Hunter, *Iowa State Coll. J. Sci.*, **15**, 215 (1941).

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

## Reactions of *cis*- and *trans*-1,2-Dibenzoylpropenes with Hydrogen Halides, Bromine and Phenylmagnesium Bromide<sup>1</sup>

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RECEIVED JULY 31, 1952

A comparison is made of the reactions of the *cis*- and *trans*-1,2-dibenzoylpropenes with hydrogen bromide and hydrogen chloride under various conditions. These propenes react with bromine in chloroform solution to form 3-(dibromomethyl)-2,5-diphenylfuran. This involves a substitution reaction with bromine, the 1,3-shift of hydrogen which has been found to be common in the reaction of the dibenzoylpropenes and similar substances, addition of the hydrogen bromide by-product and cyclization. The addition of phenylmagnesium bromide does not involve a 1,3-shift of hydrogen. The equilibria involved in these reactions are discussed.

In previous papers,<sup>3</sup> the novel reactions of *cis*- and *trans*-1,2-dibenzoylpropene (IV) with amines to give 1-amino-2,3-dibenzoylpropanes (Ic) and

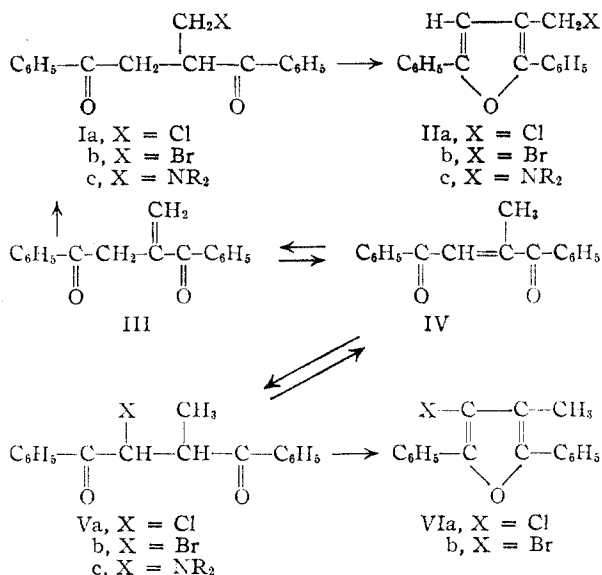
with hydrogen chloride in ether solution to give 1-chloro-2,3-dibenzoylpropane (Ia) or in chloroform solution to give 3-(chloromethyl)-2,5-diphenylfuran (IIa) were described. In these reactions, III, formed from IV by a 1,3-shift of hydrogen, is an intermediate.<sup>3b</sup>

In the present paper reactions of IV with hydrogen bromide, bromine and phenylmagnesium bromide are described. In ether solution the *trans* isomer of IV reacted with hydrogen bromide in the same manner as it did with hydrogen chloride

(1) Presented before the Organic Division at the Atlantic City Meeting of the American Chemical Society, September, 1952. This is the seventh in a series of papers dealing with 1,3-shifts of hydrogen in the reactions of dibenzoylalkenes and related compounds. For the sixth see P. S. Bailey, G. Nowlin, S. H. Pomerantz, J. V. Waggoner and E. E. Kawas, *THIS JOURNAL*, **73**, 5560 (1951).

(2) From the Ph.D. dissertation of S. H. Pomerantz.

(3) (a) R. E. Lutz and P. S. Bailey, *THIS JOURNAL*, **67**, 2229 (1945); (b) P. S. Bailey, G. Nowlin, S. H. Pomerantz, J. V. Waggoner and E. E. Kawas, *ibid.*, **73**, 5560 (1951).



to give Ib, whereas the *cis* isomer gave the corresponding furan (IIb). The structures of these new compounds were proved by conversion to the known Ic and IIc, using morpholine. This difference in behavior of the *cis* and *trans* isomers is not surprising since Lutz and McGinn<sup>4</sup> had shown previously that the *cis* isomer, with the benzoyl groups closer together in space than in the *trans* isomer, was more easily cyclized than the *trans* isomer. With very concentrated ether-hydrogen bromide solutions the *trans* isomer also gave IIb. In chloroform solution the 1,2-dibenzoylpropenes (IV) reacted with hydrogen bromide to give VIb, in contrast to their reaction with hydrogen chloride to yield IIa. In acetic acid solution both hydrogen bromide and hydrogen chloride reacted with the isomeric compounds IV to yield VI. Previously Lutz and co-workers<sup>4,5</sup> had found that these reagents reacted with IV in acetic acid solution to which acetic anhydride and sulfuric acid were added (in order to promote cyclization) to yield VI.

It is obvious from these results that the two equilibria suggested in earlier papers<sup>3</sup> are actually in force. The first equilibrium is a fast reaction to give the relatively unstable<sup>3b</sup> compounds V. Under conditions which favor cyclization of V, the essentially irreversible reaction to give VI occurs before the other equilibrium, between IV and III, can become established. This is the case with the hydrogen halides in acetic acid and acetic acid plus acetic anhydride and sulfuric acid, and with hydrogen bromide in chloroform, but not with hydrogen chloride in chloroform, the hydrogen halides in ether or with amines. In the latter cases the additions occur with III to give the more stable compounds I.

The results show that hydrogen chloride in chloroform promotes cyclization, since over a period of time (the reaction usually requires several days) IIa is formed instead of Ia, but not to the extent that does hydrogen bromide in chloroform which causes the cyclization of Vb before IV can establish equilibrium with III. Also hydrogen bromide

in ether seems to promote cyclization more than hydrogen chloride in ether; the contrast is not as great as in chloroform, however, and is noticeable only with the more easily cyclized *cis* isomer of IV. It is also worthy of note, along with these observations, that hydrogen iodide has long been used as an effective furanizing agent.<sup>6</sup>

The roles that the solvent and the hydrogen halides play in the above cyclizations is intriguing. There is a definite correlation between these results and the results of studies concerning the addition of hydrogen halides to olefinic double bonds. In the latter case the ease of reaction is in the order HI > HBr > HCl<sup>7</sup> and the reactions occur more readily in solvents such as heptane and chloroform than in ether, alcohol or water.<sup>7,8</sup> It is known that furanizations are promoted by at least three things: acidic conditions, dehydrating conditions and conditions which favor the formation of an enol intermediate.<sup>9</sup> It appears to be a hydrogen ion catalyzed reaction. As far as the solvents are concerned, the difference in the course of reaction is probably due on the one hand to the greater availability of hydrogen ions in chloroform solution than in ether solution, where essentially only oxonium type ions are present, and on the other hand to the greater dehydrating power of acetic acid than ether as well as the availability of hydrogen ions from acetic acid itself. The greater ease with which hydrogen bromide promotes furanization than does hydrogen chloride is probably due to the greater polarizability of bromides than chlorides. With hydrogen halides, this induction effect would certainly be expected to show up more in a solvent like chloroform which does not promote ionization than with a solvent like ether which associates with hydrogen ions.

When the *cis*- and *trans*-1,2-dibenzoylpropenes (IV) were treated with bromine in chloroform solution the major product, after 24 hours, was 3-(dibromomethyl)-2,5-diphenylfuran (XII). When the reaction was worked up after shorter periods of time, difficultly separable mixtures of XII and 3-bromo-4-(bromomethyl)-2,5-diphenylfuran (XI) were obtained. The *cis* isomer of IV reacted faster than the *trans* isomer. The structure of XI was proved by independent synthesis involving the bromomethylation of 3-bromo-2,5-diphenylfuran (XIII), and the structure of XII was demonstrated by hydrolysis to the known 3-formyl-2,5-diphenylfuran (XIV).

The formation of these compounds in the preceding reactions cannot be explained without assuming a substitution reaction involving bromine. The most logical course of the reaction is shown in the accompanying diagram. It consists, first, in the formation of VII by the bromination of IV at the reactive allylic methyl group, followed by a reaction of VII along two different paths, each

(6) R. E. Lutz and C. J. Kibler, *ibid.*, **61**, 3010 (1939), and numerous other papers of R. E. Lutz.

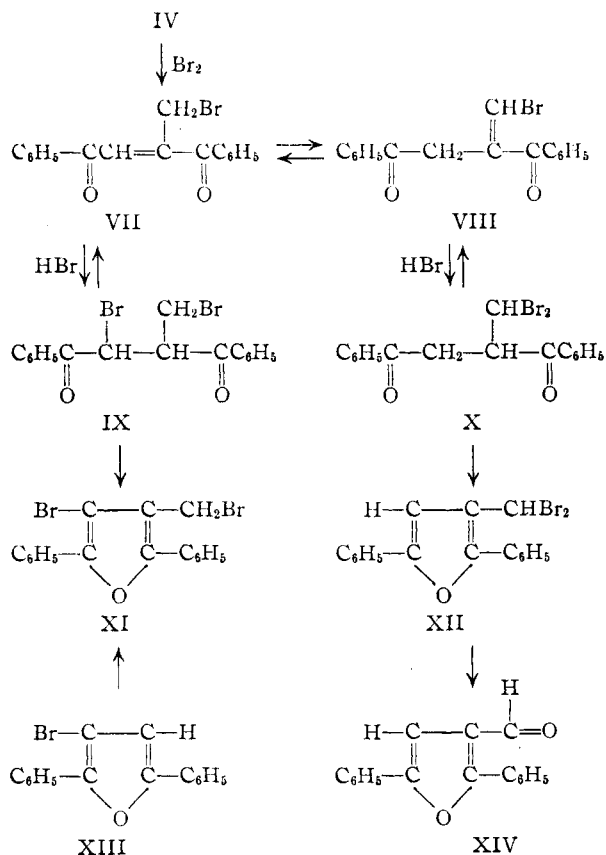
(7) R. C. Fuson, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 49-50.

(8) E. R. Alexander, "Principles of Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 138.

(9) R. E. Lutz and W. G. Reveley, *This Journal*, **61**, 1854 (1939); R. E. Lutz and F. N. Wilder, *ibid.*, **56**, 1193 (1934); R. E. Lutz, *ibid.*, **48**, 2916 (1926).

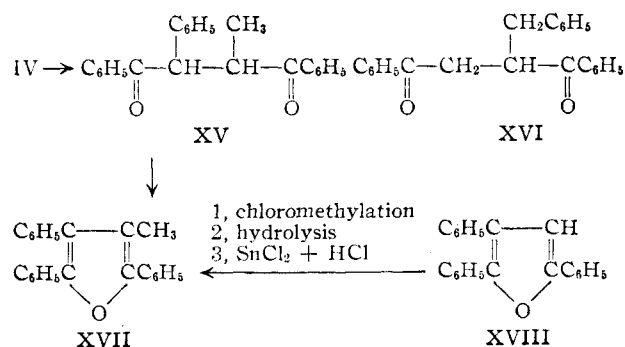
(4) R. E. Lutz and C. E. McGinn, *This Journal*, **64**, 2585 (1942).

(5) R. E. Lutz and A. H. Stuart, *ibid.*, **59**, 2316 (1937).



of which involves the addition of the hydrogen bromide by-product, to form XI and XII. In the first case the hydrogen bromide adds directly to VII forming IX which can then cyclize to XI or revert back to VII. The second path involves a 1,3-shift of hydrogen in VII to form VIII followed by the addition of hydrogen bromide to yield X, when then cyclizes to XII. By analogy to the hydrogen halide additions to IV, the equilibrium leading to IX would be expected to be fast, whereas the equilibrium between VII and VIII would be slow. Thus, in the early stages of reaction the product would be richer in XI than XII; such mixtures were found to be difficult to separate. After a period of time the equilibrium between VII and VIII becomes important and the product becomes richer in XII which was found to be more easily separated and purified than XI.

The reaction between *trans*-1,2-dibenzoylpropene (IV) and phenylmagnesium bromide gave as the only isolable product 3-methyl-2,4,5-triphenylfuran



(XVII) in poor yield. No crystalline product could be obtained from the *cis* isomer. The structure of XVII was proved by independent synthesis from 2,3,5-triphenylfuran (XVIII). This involved chloromethylation, which apparently yielded the hydroxymethyl product through hydrolysis, and reduction of the hydroxymethyl compound to XVII by means of stannous chloride and hydrochloric acid.

By analogy to the hydrogen halide reactions the formation of XV and XVII is to be expected. The reaction leading to XV would be faster than the reaction leading to XVI through intermediate III. Unlike the situation in the hydrogen halide reactions, an equilibrium between XV (or its enol) and IV would not be expected to exist since this would involve the rupture of a carbon-carbon bond.

### Experimental<sup>10</sup>

**Reaction of *cis*- and *trans*-1,2-Dibenzoylpropene (IV) with Hydrogen Bromide.** (a) *trans* Isomer in Ether Solution. 1-Bromo-2,3-dibenzoylpropane (Ib).—To a solution of dry hydrogen bromide in 200 ml. of ether (passed in 75 minutes) was added 7.5 g. of the *trans* isomer and the resulting solution was allowed to stand for 22 hours after which it was evaporated under reduced pressure. The residue weighed 8.7 g. (88%) and melted at 75–82°; recrystallized from ethanol, m.p. 84–85°. The compound was identified by conversion to known 1,2-dibenzoyl-3-(4-morpholinyl)propane<sup>3</sup> using morpholine in ether solution (m.p. 84–85°, identified by the mixture melting point method).

*Anal.* Calcd. for  $\text{C}_{17}\text{H}_{15}\text{BrO}_2$ : C, 61.65; H, 4.57. Found: C, 62.19; H, 4.36.

(b) *cis* Isomer in Ether Solution. 3-(Bromomethyl)-2,5-diphenylfuran (IIb).—When the above procedure was carried out on the *cis* isomer a 65% yield of material melting at 79–84° (m.p. 94–95° after recrystallization from 60–68° Skellysolve) was obtained. The compound was identified by conversion to known 3-(4-morpholinylmethyl)-2,5-diphenylfuran hydrochloride (m.p. 218–221°, identified by mixture melting point with a known sample<sup>3</sup>).

*Anal.* Calcd. for  $\text{C}_{17}\text{H}_{13}\text{BrO}$ : C, 65.17; H, 4.18. Found: C, 65.40; H, 4.31.

The bromomethylfuran (IIb) was also obtained in 76% yield from the *trans* isomer when a very concentrated hydrogen bromide–ether solution was used (passed 7 hours into 100 ml. of ether).

(c) **In Chloroform Solution.**—To 50 ml. of a saturated solution of hydrogen bromide in chloroform was added 2.5 g. of the *trans* isomer and the solution was set aside for 20 hours. Upon evaporation, a green oil was obtained which crystallized from Skellysolve (b.p. 90–100°), 1.9 g. (62%), m.p. 70–73°, identified as 3-bromo-2,5-diphenyl-4-methylfuran (VIb) by a mixture melting point with a known sample.<sup>5</sup> Similar results were obtained with the *cis* isomer.

(d) **In Glacial Acetic Acid.**—A mixture of 7.5 g. of the *trans* isomer in 15 ml. of 30% hydrogen bromide–acetic acid solution was set aside for 22 hours after which it was poured onto ice. The green oily layer was crystallized from Skellysolve (b.p. 60–67°) yielding 6.6 g. of material melting from 60–73°, m.p. 71–73° after recrystallization, identified as 3-bromo-2,5-diphenyl-4-methylfuran<sup>5</sup> (VIb) by the mixture melting point method. Similar results were obtained with the *cis* isomer.

**Reaction of IV with Hydrogen Chloride in Glacial Acetic Acid.**—To a solution of 7 g. of dry hydrogen chloride in 96 g. of glacial acetic acid was added 2.5 g. of the *trans* isomer. The resulting solution was allowed to stand for 21 hours, after which it was poured into water. Extraction with ether, evaporation of the ether extract, and trituration of the residue with ethanol gave 2.2 g. (83%) of material melting at 60–72°, recrystallized from ethanol, m.p. 79–80°.

(10) All melting points of pure products are corrected. Some of the microanalyses were done by Clark Microanalytical Laboratory, Urbana, Illinois.

identified as 3-chloro-2,5-diphenyl-4-methylfuran (VIa) by a mixture melting point with a known sample.<sup>5</sup>

**Reaction of Bromine with IV. (a) 3-(Dibromomethyl)-2,5-diphenylfuran (XII).**—A solution of 1 g. of *trans*-1,2-dibenzoylpropene (IV) in 25 ml. of chloroform was mixed with a solution of 0.64 g. of bromine in 30 ml. of chloroform. After 24 hours the chloroform was evaporated by a stream of air, leaving a gummy solid. During the evaporation white fumes indicative of hydrogen bromide were noted. The material was crystallized from isopropyl alcohol yielding 0.75 g. (m.p. 116–123°). Two recrystallizations from Skellysolve (b.p. 90–100°) raised the m.p. to 127–128°.

*Anal.* Calcd. for C<sub>17</sub>H<sub>12</sub>Br<sub>2</sub>O: C, 52.07; H, 3.09; Br, 40.80. Found: C, 52.42; H, 3.23; Br, 40.28.

Similar results were obtained with the *cis* isomer of IV.

**(b) 3-Bromo-4-(bromomethyl)-2,5-diphenylfuran (XI).**—In the above reactions the bromine color disappeared in about 5 minutes with the *cis* isomer and in about 45 minutes with the *trans*. Therefore, in a number of experiments the reaction mixture was worked up after periods of 10 minutes to one hour with the *cis* isomer and periods of 45 minutes to 3 hours with the *trans* isomer. In several cases with the *trans* isomer a 30–40% yield of a substance melting at 67–80° (recrystallized from isopropyl alcohol, m.p. 91–92°) was obtained. In most cases, however, bad mixtures which apparently consisted of this substance (XI) and XII were obtained.

*Anal.* Calcd. for C<sub>17</sub>H<sub>12</sub>Br<sub>2</sub>O: C, 52.07; H, 3.09; Br, 40.80. Found: C, 51.95; H, 3.24; Br, 41.13.

**Proof of Structure of 3-(Dibromomethyl)-2,5-diphenylfuran (XII).**—To a solution of 0.34 g. of 85% potassium hydroxide in 30 ml. of ethanol and 10 ml. of water was added 1 g. of 3-(dibromomethyl)-2,5-diphenylfuran (XII). The solution was warmed on a steam-bath for 5–10 minutes, during which time a red solution formed. After 15 minutes the solution was poured into water, extracted with ether and the ether extract evaporated. The aqueous layer gave a positive test for halogen. The residual oil from the ether extract crystallized from ethanol; 0.18 g. (28%), m.p. 87–90°; recrystallized from ethanol; m.p. 89.5–91°. A mixture melting point with known 2,5-diphenyl-3-formylfuran<sup>11</sup> (XIV) was 90–91°.

**Proof of Structure of 3-Bromo-4-(bromomethyl)-2,5-diphenylfuran (XI).**—3-Bromo-2,5-diphenylfuran<sup>12</sup> (XIII) was bromomethylated according to the general directions for bromomethylation given by Lutz and Bailey,<sup>13</sup> using 2 g. of XIII, 20 ml. of glacial acetic acid, 0.3 g. of paraformaldehyde and 10 ml. of 30–32% hydrogen bromide-glacial acetic acid reagent for 24 hours. The product was crystallized from isobutyl alcohol; 1.3 g. (50%), m.p. 70–80°; recrystallized (isobutyl alcohol); m.p. 90–92°. This material was shown by a mixture melting point to be identical with the material obtained by reaction of bromine with IV.

**Addition of Phenylmagnesium Bromide to IV. 3-Methyl-2,4,5-triphenylfuran (XVII).**—To a solution of 5 g. of *trans*-

1,2-dibenzoylpropene (IV) in 100 ml. of dry ether was added, with stirring, over 20 minutes, 23 ml. of 1.0 *N* phenylmagnesium bromide solution. A yellowish precipitate formed immediately and did not redissolve. After 10 minutes ice, water and hydrochloric acid were added. The ether layer was separated, aqueous phase was extracted with ether and the ether extracts were washed and evaporated. The oily residue (7 g.) crystallized from isopropyl alcohol with difficulty, yielding 0.7 g. of crystals melting at 85–121°. Trituration with isopropyl alcohol and recrystallizations from isobutyl alcohol raised the melting point to 121–122°.

*Anal.* Calcd. for C<sub>23</sub>H<sub>18</sub>O: C, 89.00; H, 5.84. Found: C, 88.89; H, 5.63.

When the experiment was carried out with the *cis* isomer, no crystalline product could be isolated. Likewise, only resins were obtained when IV (*cis* or *trans*) was added to 3 mole excess phenylmagnesium bromide in dilute ether solution.

**Proof of Structure of 3-Methyl-2,4,5-triphenylfuran (XVII). (a) Attempted Chloromethylation.**—Into a suspension of 0.31 g. of paraformaldehyde in 9 ml. of glacial acetic acid was passed dry hydrogen chloride until the paraformaldehyde dissolved. Next was added 0.8 ml. of sirupy phosphoric acid, 3 g. of 2,3,5-triphenylfuran<sup>14</sup> (XVIII) and 6 ml. of glacial acetic acid. The mixture was stirred at 45° for 13 hours, during which time solution occurred and a new precipitate formed; yield 3.4 g., m.p. 120–128°; recrystallized from acetone, m.p. 124–133°. Since the material gave a negative chloride test in a sodium fusion, it was thought to be 3-hydroxymethyl-2,4,5-triphenylfuran. It was reduced without further purification.

**(b) Reduction.**—To refluxing solution of 6 ml. of glacial acetic acid, 4 ml. of concentrated hydrochloric acid and 5 g. of stannous chloride dihydrate was added a hot solution of 0.7 g. of the crude 3-hydroxymethyl-2,4,5-triphenylfuran in 6 ml. of glacial acetic acid. The resulting solution was refluxed for 10 minutes, poured into 80 ml. of ice-water and extracted with ether. The ether extract was washed and evaporated and the residual oil was crystallized from isopropyl alcohol; yield 0.3 g., m.p. 85–112°; recrystallized from isobutyl alcohol, m.p. 118–120°. This material was shown by a mixture melting point to be identical with the substance obtained from phenylmagnesium bromide addition to IV.

**Acknowledgment.**—The authors gratefully acknowledge a grant-in-aid from the Research Corporation (to P. S. B.), a University of Texas Graduate School Scholarship (to S. H. P.) and a Pan American Refining Corporation Fellowship (to S. H. P.), which helped make this work possible.

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(14) Prepared from 1,2-dibenzoyl-1-phenylethylene (C. F. H. Allen and H. B. Rosener, *ibid.*, **49**, 2110 (1927)) by the stannous chloride, hydrochloric acid, acetic acid reduction of R. E. Lutz and R. J. Rowlett, *ibid.*, **70**, 1360 (1948); m.p. 92–94° (92–93° reported by F. R. Japp and C. I. Burton, *J. Chem. Soc.*, **51**, 431 (1887)).

(11) P. S. Bailey and R. E. Lutz, *THIS JOURNAL*, **67**, 2232 (1945).

(12) R. E. Lutz and F. N. Wilder, *ibid.*, **56**, 1193 (1934).

(13) R. E. Lutz and P. S. Bailey, *ibid.*, **68**, 2002 (1946).