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

SOME ADDITION AND CYCLIZATION REACTIONS OF 1,4-DIBENZOYL-1,3-BUTADIENE[1]

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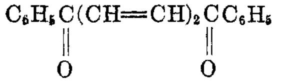
Received April 1, 1955

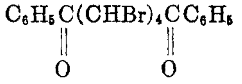
An earlier paper (1) described the synthesis of 1,4-dibenzoyl-1,3-butadiene (I), its catalytic hydrogenation, its reduction with zinc and hydrochloric acid, its reaction with diazomethane, and its dimerization in the presence of sunlight. In the present paper the reactions of I with bromine, hydrogen bromide, hydrogen chloride, morpholine, phenylmagnesium bromide, and phenyllithium are described. Two of these involve cyclizations.

The reaction with bromine yielded the tetrabromo derivative (II). All efforts to control the reaction so as to obtain a dibromo derivative failed. Hydrogen bromide and hydrogen chloride in ether, morpholine, and phenylmagnesium bromide in ether reacted with I by means of two conjugate additions to give the corresponding 1,4-dibenzoyl-2,3-disubstituted butanes (III). No evidence for 1,6-additions was obtained.



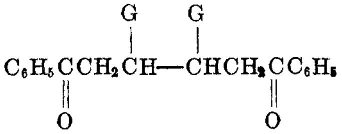
$C_6H_5\underset{O}{\underset{\|}{C}}(CH{=}CH)_2\underset{O}{\underset{\|}{C}}C_6H_5$

I



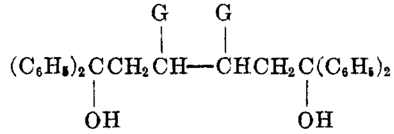
$C_6H_5\underset{O}{\underset{\|}{C}}(CHBr)_4\underset{O}{\underset{\|}{C}}C_6H_5$

II



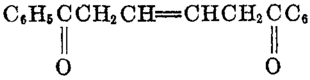
$C_6H_5\underset{O}{\underset{\|}{C}}CH_2\overset{G}{\overset{|}{C}H}—\overset{G}{\overset{|}{C}H}CH_2\underset{O}{\underset{\|}{C}}C_6H_5$

III (a) G = Cl
(b) G = Br
(c) G = NC_4H_8O
(d) G = Phenyl



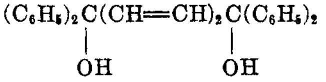
$(C_6H_5)_2\underset{OH}{\underset{|}{C}}CH_2\overset{G}{\overset{|}{C}H}—\overset{G}{\overset{|}{C}H}CH_2\underset{OH}{\underset{|}{C}}(C_6H_5)_2$

IV (a) G = H
(b) G = Phenyl



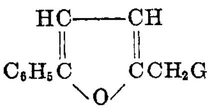
$C_6H_5\underset{O}{\underset{\|}{C}}CH_2CH{=}CHCH_2\underset{O}{\underset{\|}{C}}C_6H_5$

V

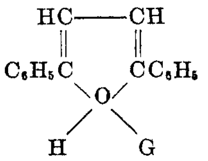


$(C_6H_5)_2\underset{OH}{\underset{|}{C}}(CH{=}CH)_2\underset{OH}{\underset{|}{C}}(C_6H_5)_2$

VI



VII (a) G = H
(b) G = Benzoyl



VIII (a) G = H
(b) G = Benzoyl

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[1] Taken from parts of the Ph.D. dissertations of W. W. H. (May, 1951) and H. W. B. (January, 1955). This work was partially supported by a grant-in-aid from the Research Corporation, New York, N. Y. One of us (W. W. H.) is grateful to the Syrian government for sponsoring his education in the United States.

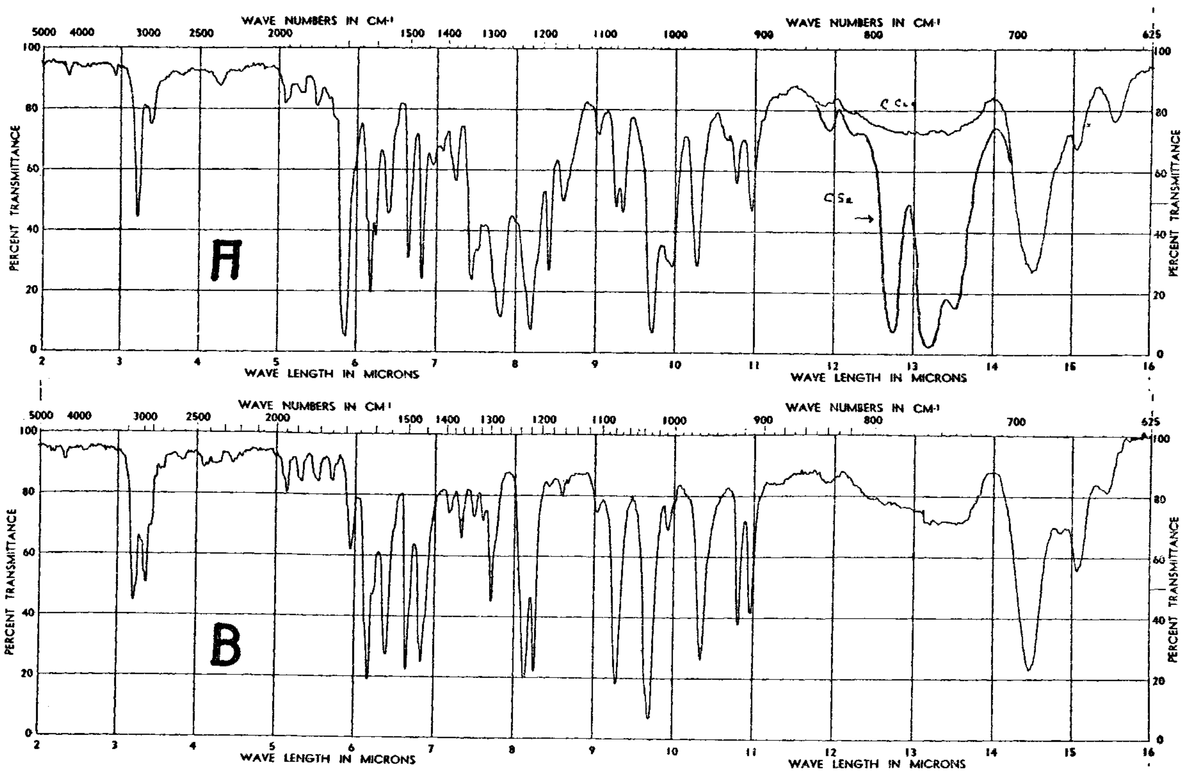

FIGURE 1. INFRARED SPECTRA OF: A, 2-Phenacyl-5-phenylfuran (VIIb); B, 2-Methyl-5-phenylfuran (VIIa). Baird spectrophotometer with NaCl prism. Solvent, carbon tetrachloride.[2]

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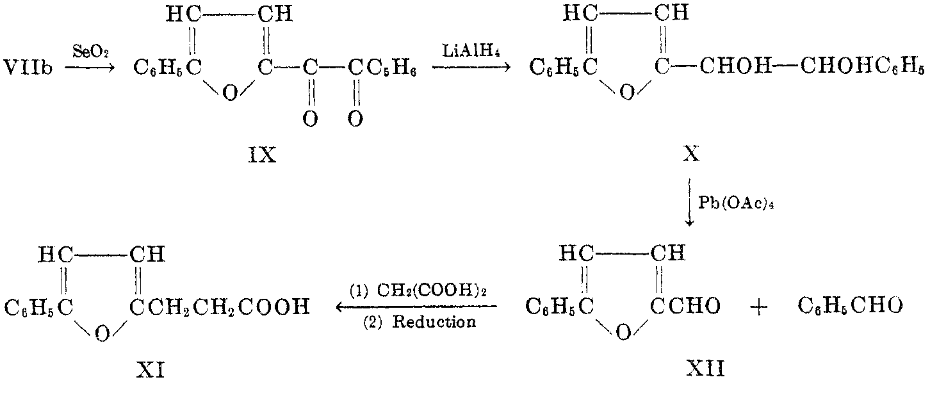
[2] All melting points are corrected. Several of the analyses were performed by Clark Microanalytical Laboratory, Urbana, Illinois. The infrared spectra were kindly furnished by Samuel P. Sadtler and Son, Inc., Philadelphia, Pennsylvania.

The dibenzoyldiphenylbutane (IIId) obtained from the Grignard reagent addition in diethyl ether is a known compound. Both it and its stereoisomer were previously obtained by the dimolecular reduction of benzalacetophenone (2).

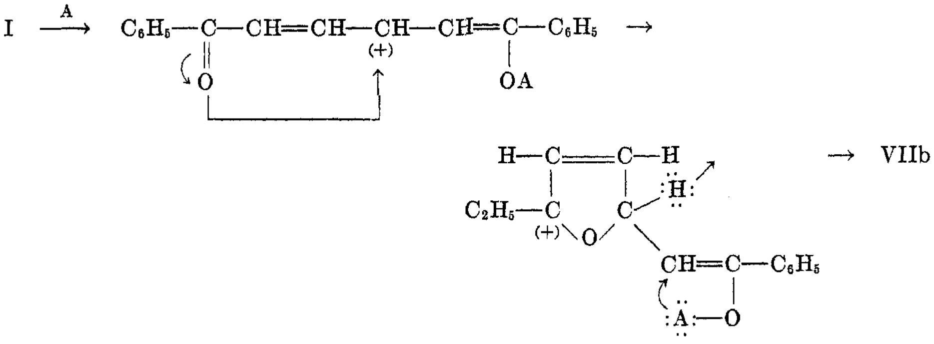
The structures of the hydrogen halide addition products (III a and b) were proven by dehydrohalogenation back to I by means of triethylamine (in case of IIIb) and by zinc dust dehalogenation to the known 1,4-dibenzoyl-2-butene (V) (1) (in case of both IIIa and IIIb). Evidence for the structure of the morpholine addition product consisted of deamination back to I with acetic acid. Only with a simple addition product would this be possible. By analogy to the additions described above the morpholinyl groups are assumed to be at the 2 and 3 positions of the butane chain.

Treatment of dibenzoylbutadiene (I) with hydrogen bromide in acetic acid or with hydrogen chloride in chloroform caused cyclization to a new substance, 2-phenacyl-5-phenylfuran (VIIb), the structure of which was demonstrated as follows. The elementary analyses and the molecular weight determination showed the compound to be isomeric with I. However, the formation of a monooxime with excess hydroxylamine indicated the presence of only one carbonyl group. Oxidation with potassium permanganate yielded benzoic acid plus (in one instance) a small amount of acetophenone. The formation of the latter substance is good evidence for the presence of the phenacyl group. It probably arose from the oxidation of VIIb to yield the anhydride of benzoic and benzoylacetic acids followed by hydrolysis, with benzoylacetic acid being an intermediate. The presence of the furan ring as well as the phenacyl group was proven by selenium dioxide oxidation of the active methylene group of VIIb to produce IX, followed by lithium aluminum hydride reduction of IX to X and lead tetraacetate oxidation of X to benzaldehyde and 5-phenyl-2-furfural (XII). The structure of XII then was proven by its conversion to the known 3-(5-phenyl-2-furyl)propanoic acid (XI) (3) through condensation with malonic acid followed by reduction of the unsaturated intermediate with sodium amalgam.

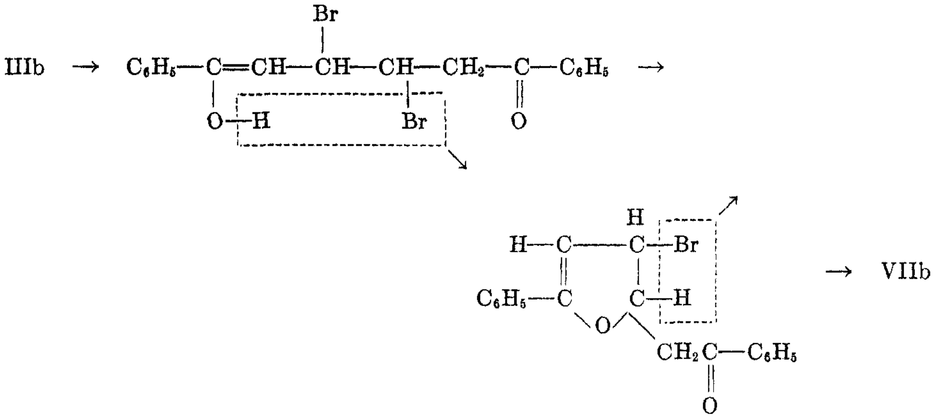
In addition to the preceding chemical proof, it is worthy of mention that a comparison of the infrared spectra of VIIb and 2-methyl-5-phenylfuran (VIIa) showed many bands in common. (See Fig. 1).



The phenacyl furan (VIIb) also was obtained by treatment of I with acetic acid alone or (in low yield) with aluminum chloride in chloroform, and by treatment of 1,4-dibenzoyl-2,3-dibromobutane (IIIb) (but not the dichloro analog, IIIa) with hot acetic acid or with acetone in the presence of activated charcoal. The ability of aluminum chloride to bring about the cyclization of I to VIIb is indicative of a general acid-catalyzed mechanism, as shown in the following scheme where A represents a "Lewis acid" such as aluminum chloride, or a hydrogen ion.



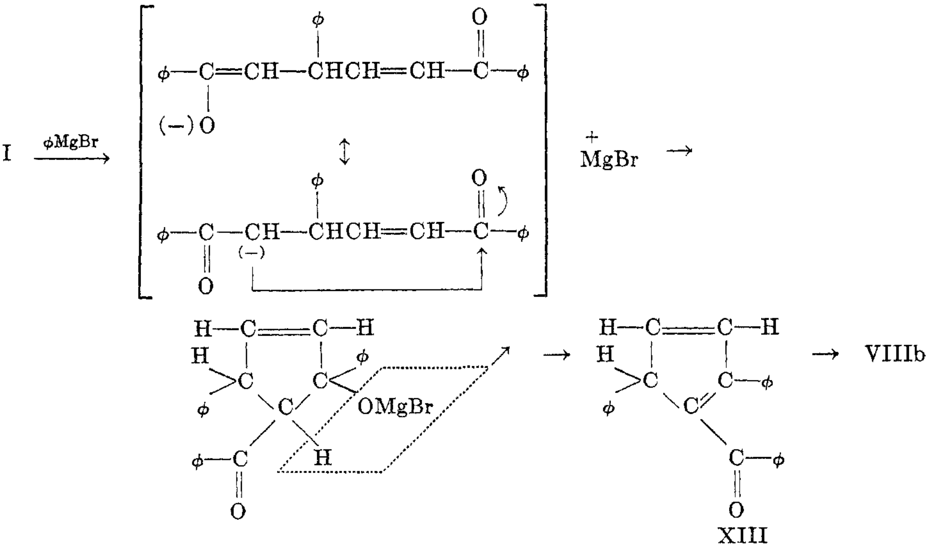
A plausible path for the conversion of IIIb to VIIb is as follows.



It is interesting to note that cyclization of I to VIIb occurs with hydrogen chloride in chloroform, but not in ether. This phenomenon was also noted in the reaction of *trans*-1,2-dibenzoylpropene with hydrogen halides. In ether, 3-halo-1,2-dibenzoylpropanes were formed, whereas in chloroform, cyclization to furans occurred (4). The explanation of these facts is probably that both these cyclizations are acid-catalyzed and that hydrogen ions are more readily available in chloroform solution than in ether where they are tied up as oxonium ions.

When the reaction of dibenzoylbutadiene (I) with phenylmagnesium bromide was carried out at 60° in dibutyl ether, a difficultly separable mixture consisting of both isomeric 1,4-dibenzoyl-2,3-diphenylbutanes (IIId) and a new substance formulated as 5-benzoyl-1,4-diphenyl-1,3-cyclopentadiene (VIIIb) was obtained. The cyclopentadiene also was obtained as one of the products of the reaction between dibenzoylbutadiene (I) and phenyllithium. The other product was 1,1,6,6-tetraphenyl-2,4-hexadiene-1,6-diol (VI), formed by two 1,2-additions, as expected. Although Grignard reagents often undergo 1,4-additions, the corresponding lithium reagents generally undergo only 1,2-additions. The structure of VI was proven by catalytic reduction to the known 1,1,6,6-tetraphenyl-1,6-hexanediol (IVa) (5).

The basis for the structure assigned to VIIIb was its elementary analyses which showed it to be the product of the addition of one mole of Grignard reagent followed by the loss of one molecule of water (or MgBrOH), its ready absorption of two moles of hydrogen during catalytic reduction at atmospheric pressure, its production of only a monoxime upon treatment with excess hydroxylamine, and the well known fact that saturated 1,6-diketones readily undergo an intramolecular condensation in the presence of basic reagents to form cyclopentene derivatives (6, 2). In the present case, cyclization occurs after the addition of only one mole of Grignard reagent to I and the result is therefore a cyclopentadiene derivative. Since the Grignard reagent is basic, this intramolecular condensation is a logical competing reaction with that leading to the dibenzoyldiphenylbutanes (IIId). As shown in the following chart the reaction should lead initially to XIII instead of VIIIb. Analogy would lead one to assume, however, that XIII would isomerize to VIIIb which has the more stable conjugated system. The synthesis of 1,4-diphenyl-1,3-cyclopentadiene (VIIIa) by the condensation of acetophenone with ethyl β-benzoylpropionate involves a similar spontaneous isomerization (7).



Further evidence for structure VIIIb is the fact that the infrared spectra of the new compound and 1,4-diphenyl-1,3-cyclopentadiene (VIIIa) are very

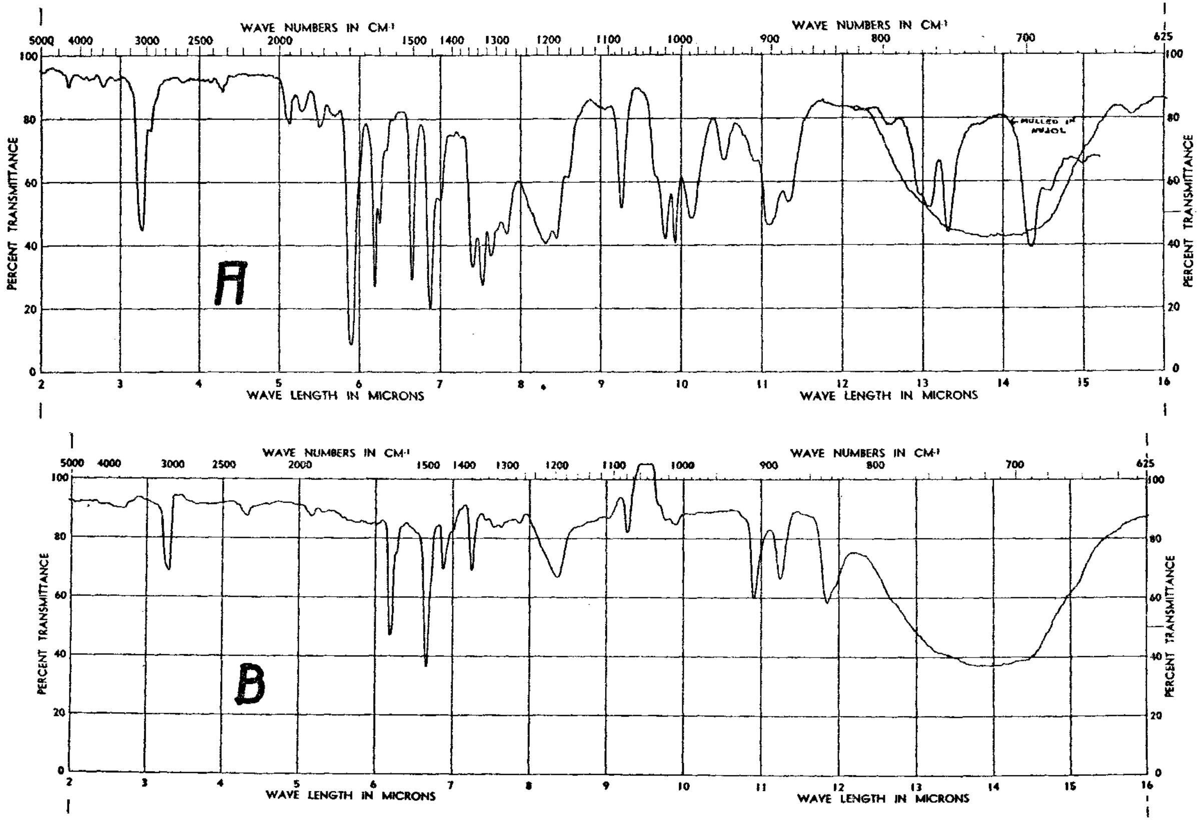


FIGURE 2. INFRARED SPECTRA OF: A. 5-Benzoyl-1,4-diphenyl-1,3-cyclopentadiene (VIIIb); B, 1,4-Diphenyl-1,3-cyclopentadiene (VIIIa). Baird spectrophotometer with NaCl prism. Solvent, chloroform.[2]

similar, differing principally in the presence of a carbonyl band at 5.9 microns in the spectrum of the new compound (see Fig. 2). Attempts to synthesize the new substance (VIIIb) from 1,4-diphenyl-1,3-cyclopentadiene (VIIIa) failed, however, due to the surprising inactivity of the hydrogens of the methylene group of VIIIa.

EXPERIMENTAL[2]

1,4-Dibenzoyl-1,2,3,4-tetrabromobutane (II). A solution of 3 g. (0.11 mole) of 1,4-dibenzoyl-1,3-butadiene (I) and 10 g. (0.062 mole) of bromine in 100 ml. of chloroform was left at room temperature for 2 hours, after which time the solution was washed with sodium bisulfite and with water, dried, and evaporated under reduced pressure. Four grams (62% yield) of material melting at 164° (decomp.) was obtained; recrystallized from acetic acid and from ethyl alcohol, m.p. 172°. The substance gave a negative unsaturation test with potassium permanganate.

Anal. Calc'd for $C_{18}H_{14}Br_4O_2$: C, 37.15; H, 2.42; Br, 54.93.
Found: C, 37.27; H, 2.69; Br, 55.22.

When a mixture of equal molar amounts of I and bromine in chloroform was used, an intractable oil was obtained. In acetic acid a mixture of starting material and the tetrabromo compound (II) was obtained.

1,4-Dibenzoyl-2,3-dibromobutane (IIIb). To a suspension of 4 g. of dibenzoylbutadiene (I) in 120 ml. of absolute ether at 0° was added 35 g. of 30% hydrobromic acid–acetic acid reagent. The mixture was kept cold for an hour, after which time it was filtered and the resulting crystals were washed several times with ether and with water, and recrystallized from acetone. The substance (3.5 g., 55% yield) melts with decomposition at about 154° (if placed in bath preheated to about 145°, otherwise it decomposes around 117°).

Anal. Calc'd for $C_{18}H_{16}Br_2O_2$: C, 50.97; H, 3.80; Br, 37.68.
Found: C, 50.96; H, 3.59; Br, 37.58.

Treatment of IIIb with hot triethylamine converted it back to I (identification by mixture melting point).

1,4-Dibenzoyl-2,3-dichlorobutane (IIIa). Dry hydrogen chloride was passed into 100 ml. of absolute ether for one hour at 0°, after which time 2 g. of dibenzoylbutadiene (I) was added and the mixture was set aside for 2 hours. The resulting solution was evaporated and the residue was triturated with ethyl alcohol at room temperature; yield 1.2 g. (48%), m.p. 135–140°; recrystallized from ethyl alcohol and from isopropyl alcohol, m.p. 147–148°; positive Beilstein test for halogen.

Anal. Calc'd for $C_{18}H_{16}Cl_2O_2$: C, 64.49; H, 4.81.
Found: C, 64.46; H, 4.95.

Conversion of 1,4-dibenzoyl-2,3-dihalobutanes (IIIa and b) *to 1,4-dibenzoyl-2-butene* (V). A mixture of 3 g. of the dibromo compound (IIIb), 1.5 g. of zinc dust, 4.5 g. of sodium iodide, and 25 ml. of acetone was refluxed for 3 hours after which time it was filtered and the filtrate was cooled, yielding 1 g. of colorless crystals melting at 134–136° after recrystallization from ethyl alcohol. A mixture melting point with known 1,4-dibenzoyl-2-butene (m.p. 135–136°) (1) was not depressed. Similar results were obtained with the dichloro compound (IIIa).

1,4-Dibenzoyl-2,3-di-(4-morpholinyl)butane (IIIc). One gram of dibenzoylbutadiene (I) was dissolved in 20 ml. of morpholine and the solution was set aside for two hours, during which time a colorless precipitate formed. The morpholine was removed under reduced pressure and the residue was triturated with hot ethyl alcohol; 1.2 g. (70%), m.p. 184–195°. The substance had a very limited solubility in most solvents. It was purified by washing with hot water, acetone, ethyl alcohol, chloroform, and benzene and by recrystallization from a large volume of ethyl alcohol; m.p. 197–198°.

Anal. Calc'd for $C_{26}H_{32}N_2O_4$: N, 6.44. Found: N, 6.73, 6.80.

Treatment of IIIc with boiling acetic acid converted it back to I (identification by mixture melting point).

1,4-Dibenzoyl-2,3-diphenylbutane (IIId). To a solution of 0.114 mole of phenylmagnesium bromide in 75 ml. of diethyl ether was added with stirring 5 g. (0.019 mole) of dibenzoylbutadiene (I) over a period of 30 minutes. The mixture then was refluxed an hour, after which it was hydrolyzed with 75 ml. of conc'd hydrochloric acid and 75 ml. of ice water. The ether layer was separated, washed, dried, and evaporated. The oily residue was extracted three times with 5-ml. portions of hot acetone (leaving 0.1 g. of unreacted I). From the cooled acetone extract 0.8 g. of material melting at 193–195° crystallized. Partial evaporation gave an additional 1.5 g.; recrystallized from ethyl alcohol, m.p. 193–195°; total yield 28%. The substance was identified as one of the isomeric 1,4-dibenzoyl-2,3-diphenylbutanes (IIId) by means of a mixture melting point with an authentic sample (2).

2-Phenacyl-5-phenylfuran (VIIb). (*a*) *Reaction of* I *with hydrogen bromide in acetic acid.* To a suspension of 3 g. of dibenzoylbutadiene (I) in 50 ml. of glacial acetic acid was added 16 g. of 30% hydrogen bromide–acetic acid reagent. After 20 minutes, during which time solution occurred, the material was poured into an aqueous sodium carbonate solution, and the resulting mixture was extracted with ether. The ether extract was washed and evaporated and the oily residue was crystallized from ethyl alcohol, yielding 1 g. (33%) of material melting at 60–64°. Several recrystallizations from 50% ethyl alcohol and from ether raised the melting point to 65–66°. The substance gave a negative Beilstein test for halogen. It decomposes slowly on standing.

Anal. Calc'd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38; M.W. 262.3.
Found: C, 82.18; H, 5.21; M.W. 266, 280 (Rast).

(*b*) *Reaction of* I *with hydrogen chloride in chloroform.* Dry hydrogen chloride was passed into 175 ml. of chloroform at 0° for 1 hour, after which time 4 g. of dibenzoylbutadiene (I) was added and the resulting solution was allowed to stand for two hours. The solution was washed, dried, and evaporated and the residue was crystallized from ethyl alcohol; 2.6 g. (65%), m.p. 61–64°; recrystallized from ethyl alcohol, m.p. 65–66°; no depression in mixture melting point with material in part (*a*). In several preparations, using both hydrogen bromide and hydrogen chloride, the crude product melted as low as 49–52°. This material gave with hydroxylamine the same product as that obtained from I (m.p. 235–237°) and different from that obtained from pure VIIb (m.p. 135–138°). It is thought to be a stereoisomer of I which cyclizes to VIIb easier than does I. It was too unstable to be analyzed, however. Recrystallization from aqueous ethyl alcohol converted it to VIIb.

Reaction of I with hydrogen chloride in acetic acid solution gave a mixture of IIIa and VIIb; identifications by mixture melting points.

(*c*) *Reaction of* I *with acetic acid.* A mixture of 1 g. of I in 15 ml. of glacial acetic acid was refluxed for one hour and then cooled in an ice bath; 0.4 g. of I was recovered. The filtrate was neutralized with sodium carbonate and the resulting mixture was extracted with ether. The ether extract was washed, dried and evaporated and the oily residue was crystallized from ethyl alcohol; 0.45 g. (75% yield based on 0.6 g. I reacting) m.p. 63–65°, no depression in mixture melting point with known VIIb.

Attempted cyclization of I using sulfuric acid in acetic anhydride or chloroform proved too drastic; only resinous materials were produced.

(*d*) *Cyclization of* I *in the presence of aluminum chloride.* Compound I (2 g.) was dissolved by shaking in a mixture of 1 g. of anhydrous aluminum chloride and dry chloroform. The mixture was set aside for 1 hour, after which time it was washed, dried, and evaporated. The residue was extracted repeatedly with ethyl alcohol. Evaporation of the extract and fractional crystallization of the residue from ethyl alcohol gave a 15% recovery of I and a 24% yield (based on amount I reacting) of VIIb (m.p. 61–65°); identifications by mixture melting point method.

(*e*) *Conversion of 1,4-dibenzoyl-2,3-dibromobutane* (IIIb) *to 2-phenacyl-5-phenylfuran* (VIIb). A solution of 0.5 g. of IIIb in 15 ml. of glacial acetic acid was heated for a few minutes, after which it was diluted with water and cooled. Crystals formed, and were filtered off and recrystallized from dilute ethyl alcohol; m.p. 64–65°, no depression in a mixture melting point with VIIb prepared in part *a*. In another instance IIIb was converted to VIIb during attempted recrystallization from acetone in the presence of activated charcoal; identification by mixture melting point method. Attempts to convert the dichloro compound (IIIa) to VIIb failed; starting material was recovered.

The *oxime* of VIIb was prepared by refluxing a mixture of 2.8 g. of VIIb, 2.8 g. of hydroxylamine hydrochloride, 15 ml. of absolute ethanol, and 15 ml. of dry pyridine for 2 hours; yield, 2.4 g., m.p. 132–136°; recrystallized from ethyl alcohol and from isopropyl alcohol, m.p. 136–137°.

Anal. Calc'd for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45; N, 5.05.
Found: C, 77.84; H, 5.77; N, 5.33.

Oxidation of 2-phenacyl-5-phenylfuran (VIIb) *with potassium permanganate.* A mixture of 2 g. of potassium permanganate, 2 g. of VIIb, and 80 ml. of water was refluxed for ½ hour after which time it was cooled and treated with sodium bisulfite. Acidification and cooling gave 0.1 g. of benzoic acid; m.p. 119–121°, no depression in mixture melting point with an authentic sample. The filtrate was steam-distilled and the distillate was extracted with ether. Evaporation of the ether extract and treatment of the residue with hydroxylamine by the usual method gave 0.04 g. of acetophenone oxime; m.p. 56–58°, no depression in mixture melting point with an authentic sample.

Selenium dioxide oxidation of VIIb *to 1-phenyl-2-(2-phenyl-5-furyl)ethanedione* (IX). A mixture of 1.3 g. (0.012 mole) of selenium dioxide, 0.2 ml. of water, and 30 ml. of dioxane was refluxed until solution occurred (2 hours), after which time 2.6 g. (0.01 mole) of VIIb was added and the resulting mixture was refluxed with stirring for 8 hours. The selenium metal was filtered from the reddish-black mixture and the dioxane was removed under reduced pressure. The residue crystallized from ethyl alcohol after 2 days in the refrigerator; yield, 2.6 g. (94%), bright yellow crystals, m.p. 84.5–86° after recrystallization from "Skellysolve B"; decomposes on exposure to light.

Anal. Calc'd for $C_{18}H_{12}O_3$: C, 78.25; H, 4.38.
Found: C, 78.02; H, 4.68.

The *quinoxaline derivative* was prepared from 0.5 g. of IX and 0.39 g. of *o*-phenylenediamine in 30 ml. of ethanol; it was stirred for 5 minutes, cooled and filtered; yield, 0.45 g., m.p. 188–196°; recrystallized from ethyl alcohol, m.p. 192–193°.

Anal. Calc'd for $C_{24}H_{16}N_2O$: C, 82.74; H, 4.63; N, 8.04.
Found: C, 82.70; H, 4.57; N, 8.22.

Conversion of IX *to 5-phenyl-2-furfural* (XII) *and benzaldehyde.* To a solution of 1.1 g. (0.029 mole) of lithium aluminum hydride in 100 ml. of absolute ether was added over a period of 20 minutes a solution of 13.8 g. (0.05 mole) of IX in 250 ml. of absolute ether. The resulting mixture was stirred for one hour, after which time it was decomposed by the cautious addition of water. The ether layer was separated, washed, dried and evaporated. The residue, assumed to be the glycol (X), resisted crystallization and was used as such in the subsequent oxidation.

To a solution of lead tetraacetate in acetic acid (prepared by dissolving, with stirring, 6.85 g. of dried red lead oxide, Pb_3O_4, in 40 ml. of glacial acetic acid) was added 2.8 g. of the crude glycol (X). The mixture was stirred for 2 hours after which time water was added and the resulting mixture was extracted with ether. The ether extract was washed, dried, and evaporated, and the residue was distilled. Much decomposition occurred. However, small amounts of benzaldehyde (b.p. 50–55°/5 mm.) and of 5-phenyl-2-furfural (XII) (b.p. 146°/5 mm.) were obtained. A portion of the latter was converted to its *oxime* the usual way; crystallized from methanol, m.p. 182–185°.

Anal. Calc'd for $C_{11}H_9NO_2$: C, 70.57; H, 4.85; N, 7.48.
Found: C, 70.57; H, 5.46; N, 7.13.

Conversion of XII *to 3-(5-phenyl-2-furyl)propionic acid* (XI). A mixture of one-half gram of XII, 0.32 g. of malonic acid, 1 ml. of pyridine, and a drop of piperidine was heated over the steam-bath for 2 hours and then poured onto 3 g. of ice and 0.5 ml. of conc'd sulfuric acid. Yellow crystals were obtained; 0.62 g. (96% yield), m.p. 163–165°. These were immediately neutralized with 10% NaOH and the resulting salt was dissolved in 20 ml. of water. To this solution was added portionwise 11 g. of 4% sodium amalgam over a period of 48 hours. The mercury then was separated, the solution was acidified with hydrochloric acid, and the resulting crystals were filtered off; 0.32 g. (64%), m.p. 111–113°; recrystallized from water and from ether, m.p. 113–115° no depression observed in a mixture melting point with known 3-(5-phenyl-2-furyl)propionic acid (m.p. 114–115°) (3).

Attempted syntheses of 2-phenacyl-5-phenylfuran (VIIb) *by alternative routes.* (*a*). Attempts to synthesize VIIb from 2-methyl-5-phenylfuran (VIIa) (8), principally through the 2-bromomethyl derivative[3] failed, apparently due to the instability of the bromo compound. Attempts to synthesize 1,6-diphenyl-1,3,6-hexanetrione by the condensation of β-benzoylpropionyl chloride with the sodium salt of ethyl benzoylacetate also failed.[4] Likewise, attempts to prepare 1,6-diphenyl-2-hexene-1,4,6-trione by the condensation of β-benzoylacrylyl chloride with the sodium salt of ethyl benzoylacetate failed; only tars were produced.

(*b*) *Ethyl δ-benzoyllevulinate.* To a mixture of 1 mole of sodium ethoxide and 192 g. (1 mole) of ethyl benzoylacetate in 125 ml. of dry benzene (which had been refluxed for an hour) was added 150 g. (1 mole) of β-carbethoxy propionyl chloride in 75 ml. of benzene. After the resulting mixture had refluxed for 2 hours it was hydrolyzed with 600 ml. of 5% sulfuric acid. The benzene layer was washed, dried, and evaporated and the residue was decarboxylated by means of 14 g. (0.06 mole) of β-naphthalenesulfonic acid monohydrate according to the method of Riegel and Lilienfeld (9). An ether solution of the decarboxylation product was washed, dried, and evaporated. Upon distillation of the residue, 50 g. (20% yield) of material boiling at 114–116°/0.5 mm. was collected; this was redistilled and the fraction boiling at 125–127°/2 mm. was analyzed.

Anal. Calc'd for $C_{14}H_{16}O_4$: C, 67.72; H, 6.50.
Found: C, 67.71; H, 6.24.

Hydrolysis gave a material the analyses of which indicated a mixture of δ-benzoyllevulinic acid and its lactone. Therefore, no attempt was made to convert the material to 1,6-diphenyl-1,3,6-hexanetrione and subsequently to VIIb.

The reaction between 1,4-diphenyl-1,3-butadiene (I) *and phenylmagnesium bromide at 60°.* To an ether solution of freshly prepared phenylmagnesium bromide (0.19 mole) was added 480 ml. of dry *n*-butyl ether, followed by 40 g. (0.15 mole) of dibenzoylbutadiene (I), added portionwise, in a nitrogen atmosphere. The mixture was stirred at 60° for 7 hours, after which time it was hydrolyzed with 600 ml. of concentrated hydrochloric acid and ice-water. During the hydrolysis 8.4 g. of a solid (A), melting at 182–188°, precipitated and was removed. The filtrate was separated and the ether layer was washed, dried, and evaporated to 100 ml., after which treatment it was cooled in an ice-bath; 20 g. of a solid (B) (m.p. 100–130°) precipitated. Evaporation of the filtrate yielded 2 g. of a third solid which, after repeated recrystallization from ethyl alcohol and chloroform, yielded 1.4 g. of the high-melting isomer of 1,4-dibenzoyl-2,3-diphenylbutane (IIId) (m.p. 264–266°). Numerous fractional recrystallizations of solid A from acetone and ethyl alcohol gave 5.4 g. and 2 g. of low-melting (188–190°) and the high-melting (264–266°) isomers of 1,4-dibenzoyl-2,3-diphenylbutane (IIId) respectively. Many fractional recrystallizations of B, using ether, ligroin, and ethyl alcohol, produced 0.2 g. and 1.5 g. of the high-melting (266–268°) and low-melting (188–190°) isomers of IIId, respectively, and 5 g. (11% yield) of a new substance which is formulated as 5-benzoyl-1,4-diphenyl-1,3-cyclopentadiene (VIIIb) (m.p. 133–134° after recrystallization from ethyl or isopropyl alcohol).

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[3] For example, conversion of the bromo group to a carboxyl group, followed by the Friedel-Crafts reaction to VIIb, or bromo group to Grignard or lithium derivative, followed by treatment with benzoyl chloride.

[4] The idea had been to cyclize the triketone to VIIb. It proved impossible, however, to convert β-benzoylpropionic acid to its acid chloride. Only resinous materials were obtained.

Anal. Calc'd for $C_{24}H_{18}O$: C, 89.41; H, 5.63.
Found: C, 89.37; H, 5.67.

The total yield of the low-melting isomer of IIId (m.p. 188–190°) was 11% and of the high-melting isomer (m.p. 266–268°) was 6% after the above described tedious separation. Identifications were by mixture melting points with authentic samples (2).

Preparation of the isomeric 1,1,3,4,6,6-hexaphenyl-1,6-hexanediols (IVb). Because the mixture obtained from the preceding experiment seemed quite complex, it was decided to prepare the isomeric diols (IVb) by reaction of the isomeric diones (IIId) with excess phenylmagnesium bromide, in order to see if these corresponded with anything found in the preceding reaction mixture.

(*a*) *Isomer of* IVb *prepared from high-melting isomer of* IIId. To a well-stirred solution of 16 ml. of ethereal phenylmagnesium bromide (0.019 mole) and 36 ml. of dry *n*-butyl ether was added 2 g. (0.0048 mole) of the high-melting (266–268°) isomer of dibenzoyldiphenylbutane (IIId). The mixture was kept at 70° for 10 hours, after which time it was hydrolyzed with 20 ml. of conc'd hydrochloric acid and ice. The ether layer was separated, washed, and cooled; 2.3 g. of a solid melting at 178–190° crystallized. Several recrystallizations from ethyl alcohol gave 1.5 g. (54% yield) of material melting at 194–195°. Marvel, Mueller, and Peppel (10) reported a melting point of 193–194° for this same material made another way. The material showed a large depression in a mixture melting point with the low-melting isomer of IIId.

Anal. Calc'd for $C_{42}H_{38}O_2$: C, 87.77; H, 6.66.
Found: C, 87.61; H, 6.68.

(*b*) *Isomer of* IVb *prepared from low-melting isomer of* IIId. By the preceding method the low-melting isomer of IIId (m.p. 188–190°) was converted in 73% yield to a new isomer of IVb which melted at 204–205° (recrystallization from isopropyl alcohol).

Anal. Calc'd for $C_{42}H_{38}O_2$: C, 87.77; H, 6.66.
Found: C, 87.61; H, 6.53.

Reaction of 1,4-dibenzoyl-1,3-butadiene (I) *with phenyllithium.* To 150 ml. of an ether solution containing 0.125 mole of phenyllithium (11) was added under nitrogen, portionwise, with stirring, 10 g. (0.04 mole) of I. Refluxing occurred. The mixture was stirred at room temperature for one hour, after which time it was hydrolyzed with 100 ml. of conc'd hydrochloric acid and ice-water. A precipitate (A) was filtered off (m.p. 165–175°). The filtrate was separated and the ether layer was washed and evaporated. The residue, weighing 4 g. and melting at 96–100°, yielded 2 g. (16% yield) of the benzoyldiphenylcyclopentadiene (VIIb) after fractional recrystallization from ether, ethyl alcohol and ligroin; m.p. 133–134°, no depression in mixture melting point with the sample obtained from the phenylmagnesium bromide reaction.

1,1,6,6-Tetraphenyl-2,4-hexadiene-1,6-diol (VI). Precipitate A (above) melted at 179–180° after several recrystallizations from ethyl and isopropyl alcohols.[5]

Anal. Calc'd for $C_{30}H_{26}O_2$: C, 86.09; H, 6.26.
Found: C, 86.11; H, 6.01.

The structure of VI was proven by catalytic reduction (Adam's catalyst) at atmospheric pressure to the known 1,1,6,6-tetraphenyl-1,6-hexanediol (IVa); 71% yield; m.p. 214–215°. Bauer and Herlzog reported a melting point of 213° (5).

Evidence for structure of 5-benzoyl-1,4-diphenyl-1,3-cyclopentadiene (VIIIb). (*a*). *Catalytic reduction.* Raney nickel in ethanol was hydrogenated until no more hydrogen was absorbed, after which time VIIIb was added. After the ready absorption of hydrogen at atmospheric pressure had ceased, it was found that 2.2 moles of hydrogen per mole of compound had been absorbed.

(*b*). *Oxime.* An oxime was prepared by the usual method using hydroxylamine hydrochloride and pyridine. A good yield of material melting at 182–184° after recrystallization from ethyl alcohol was obtained.

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[5] A geoisomer of this dialcohol is reported by Kuhn and Wallenfels (12) to melt at 147°.

Anal. Calc'd for $C_{24}H_{19}NO$: C, 85.43; H, 5.68.
Found: C, 85.13; H, 5.45.

(*c*). *Oxidation.* Oxidation with potassium permanganate in water yielded benzoic acid as the only crystalline material. Ozonolysis in chloroform at −30° gave benzoic acid and a material which reacted with *p*-nitrophenylhydrazine to give a mixture (m.p. 130–160°) which resisted all efforts toward separation.

Attempted syntheses of VIIIb *by alternate routes.* (*a*) *From 1,4-diphenyl-1,3-cyclopentadiene*[6] (VIIIa). All attempts to form a lithium, sodium, or Grignard derivative of VIIIa, from which VIIIb could be prepared by treatment with benzoyl chloride failed. In typical experiments an ether solution of phenylmagnesium bromide or phenyllithium was added to a partial solution of VIIIa in dry benzene or dioxane and the mixture was refluxed for 24 hours, after which time benzoyl chloride was added. The recovery of VIIIa varied from 20% to 66%. The remainder was a tar. When methylmagnesium iodide was employed, no evidence of methane evolution was observed. Attempts to form halo derivatives of VIIIa by treatment with N-bromosuccinimide or sulfuryl chloride by the usual methods produced tars.

(*b*) *From ethyl benzoylpropionate and dibenzoylmethane.* Attempts to synthesize VIIIb from ethyl benzoylpropionate and dibenzoylmethane by the same method used to prepare VIIIa from ethyl benzoylpropionate and acetophenone (7) failed. Only starting materials and an intractable oil were obtained.

It is interesting to note that propiophenone likewise failed to react when used in the reaction in place of acetophenone.

SUMMARY

1,4-Dibenzoyl-1,3-butadiene has been found to react predominantly by two 1,4-type conjugate additions. However, hydrogen halides and other acidic reagents under certain conditions cause cyclization to 2-phenacyl-5-phenylfuran, and either phenylmagnesium bromide or phenyllithium under certain conditions causes cyclization to 5-benzoyl-1,4-diphenyl-1,3-cyclopentadiene.

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[6] Prepared by the method of Drake and Adams (7).