+52.6°. 0.1008 g. made up to 25 cc. with glacial acetic acid at 20° gave α_D +0.56; *l*, 2; $[\alpha]^{20}_D$ +69.4°.

Anal. Calcd. for $C_{13}H_{14}OBrCl$: C, 49.12; H, 4.42. Found: C, 49.04; H, 4.04.

Decomposition of the oily fraction C in a similar manner gave *l*-acid which after two crystallizations gave a constant rotation; white crystals, m. p. 155–156° (cor.).

Rotation. (*l*-acid) 0.0994 g. made up to 25 cc. with absolute ethanol at 20° gave α_D −0.43; *l*, 2; $[\alpha]^{20}_D$ −54°.

Anal. Calcd. for $C_{13}H_{14}O_2BrCl$: C, 49.12; H, 4.42. Found: C, 49.62; H, 4.52.

Racemization Experiments.—The *d*-acid was refluxed in absolute ethanol for fifteen hours and in glacial acetic acid for twelve hours with no change in rotation in either case.

Bromination of *d*- + *l*-Acids: *dl*-β-Chloro-β-(2,4,6-trimethyl-3,5-dibromophenyl)-α-methylacrylic Acid.—The procedure for bromination was exactly that used in bromination of the racemic compound. The product was optically inactive and proved to be identical with the dibromo compound previously prepared; white needles, m. p. 228–229° (cor.). Bromination of the *l*-acid gave the same compound.

Action of Chlorosulfonic Acid on *d*- and *l*-Acids. Preparation of *d*- and *l*-β-Chloro-β-(2,4,6-trimethyl-3-bromo-5-chlorosulfonylphenyl)-α-methylacrylic Acids.—The procedure in these preparations was identical with that used for the racemic acid. Both *d*- and *l*-forms consisted of white crystals from petroleum ether (b. p. 60–100°), m. p. 183–184° (cor.).

Rotation. (derivative from *d*-acid) 0.1018 g. made up to 25 cc. with benzene at 20° gave α_D −0.07; *l*, 2; $[\alpha]^{20}_D$ −8.6°.

Anal. Calcd. for $C_{13}H_{13}O_4BrCl_2S$: C, 37.59; H, 3.13. Found: C, 37.96; H, 3.29.

Rotation. (derivative from *l*-acid) 0.1002 g. made up to 25 cc. with benzene at 20° gave α_D +0.08; *l*, 2; $[\alpha]^{20}_D$ +10.0°.

Summary

1. β-Chloro-β-(2,4,6-trimethyl-3-bromophenyl)-α-methylacrylic acid has been synthesized. This substance was resolved into its enantiomorphic forms. They proved to be very stable to racemization.

2. The asymmetry of the molecule is undoubtedly due to restricted rotation between the carbon of the benzene ring and the olefinic carbon to which it is attached. Necessity for unsymmetrical substitution in the benzene ring was demonstrated by bromination of the active acids and introduction of a chlorosulfonyl group. Bromination which results in a dibromo compound with symmetrical substitution gave an inactive product. Chlorosulfonic acid, on the other hand, which results in a molecule still containing an unsymmetrically substituted benzene, gave an optically active product.

3. This compound is typical of a general class of aryl olefins which should be capable of resolution.

URBANA, ILLINOIS RECEIVED NOVEMBER 8, 1939

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Synthesis of 1,3-Diphenyldihydroisobenzofurans, 1,3-Diphenylisobenzofurans and *o*-Dibenzoylbenzenes from the Diene Addition Products to Dibenzoylethylene

BY ROGER ADAMS AND MARVIN H. GOLD[1]

In a recent paper, the addition of 1,4-dimethylbutadiene to *trans*-dibenzoylethylene was described and a number of the reaction products of this substance was prepared.[2] A more systematic study is now under way on the diene addition products to dibenzoyl and substituted dibenzoyl ethylenes. In this communication will be reported the substances formed by the action of butadiene, 2,3-dimethylbutadiene, and cyclopentadiene on dibenzoylethylene, and the transformations of these substances.

2,3-Dimethylbutadiene and *trans*-dibenzoylethylene react to give a quantitative yield of 1,2-dimethyl-4,5-dibenzoylcyclohexene (I), which adds a mole of bromine to give the expected dibromide (II).

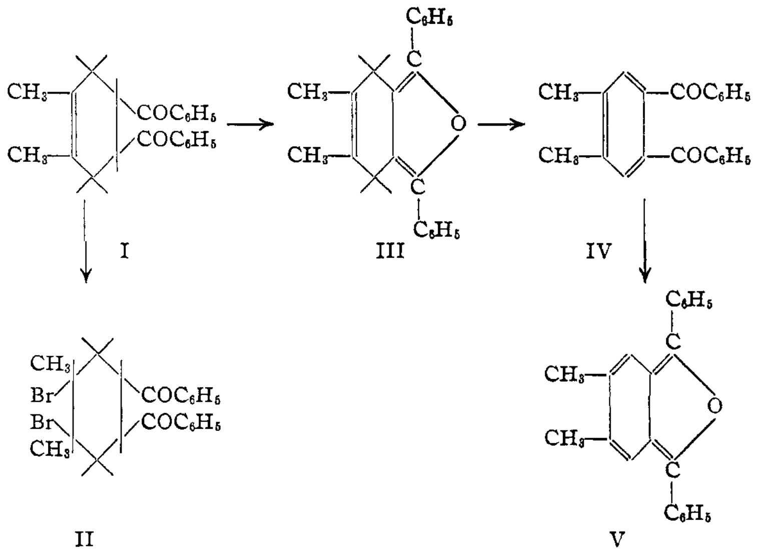
The cyclohexene (I) is converted, by means of a few drops of sirupy phosphoric acid in acetic anhydride, into 1,3-diphenyl-5,6-dimethyl-4,7-dihydroisobenzofuran (III).

Compound III, on treatment with two molecules of bromine followed by sodium acetate in acetic acid, gives an excellent yield of 1,2-dimethyl-4,5-dibenzoylbenzene (IV). The exact mechanism of this reaction was not determined but it is probable that one mole of bromine adds to the cyclohexene double bond and one mole to the 1,4-position in the furan conjugated system

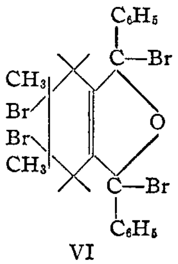
---

[1] An abstract of a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

[2] Adams and Geissman, THIS JOURNAL, **61**, 2083 (1939).



(VI). Two hydrogen bromides are then eliminated to form the benzene ring with simultaneous hydrolysis of the brominated furan ring to give two benzoyl groups.



VI

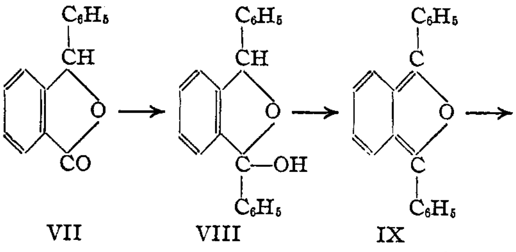
o-Dibenzoylbenzene and one or two of its derivatives have been converted into 1,3-diphenylisobenzofuran by means of zinc dust and acetic acid.[3] This reaction, however, has not been extensively studied since the isobenzofurans have been in general more easily obtained than the *o*-dibenzoylbenzenes and have served as intermediates in the preparation of the latter compounds. Since in the reactions described in this paper the *o*-dibenzoylbenzenes are more easily obtained than the isobenzofurans, the conversion of the former to the latter was investigated. It was found that activated zinc and ethanolic sodium hydroxide was a superior reagent and resulted in a quantitative conversion of IV to the 1,3-diphenyl-5,6-dimethylisobenzofuran (V). The time of reduction of the *o*-dibenzoylbenzenes varies with the activity of the zinc dust.

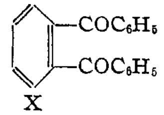
If the product formed by the addition of one molecule of bromine to compound III was isolated and then treated with sodium acetate, a mixture of the *o*-dibenzoylbenzene (IV) and the isobenzofuran (V) was obtained.

Butadiene in place of 2,3-dimethylbutadiene adds equally well to *trans*-dibenzoylethylene and by analogous reactions to those just described, compounds corresponding to I, II, III, IV, and V without the methyl groups were synthesized.

o-Dibenzoylbenzene and certain of its derivatives are known compounds but none of the methods of preparation is entirely satisfactory. A brief review of these methods is pertinent. It was first prepared by oxidation of *o*-dibenzylbenzene resulting as one of the products from the action of zinc dust on a mixture of benzyl chloride and benzene.[4] Beis[5] obtained it as one of the products from the reaction of phenylmagnesium bromide on N-phenylphthalimide. Bruhat and Thomas[6] used the Grignard reagent from *o*-diiodobenzene and two moles of benzonitrile followed by hydrolysis. Blicke and Patelski[3b,7] condensed *o*-benzoylbenzonitrile with phenylmagnesium bromide followed by hydrolysis. Clar, John and Hawran[8] replaced the two chlorines in *o*-phthalyl chloride with phenyl groups by the action of phenylmagnesium bromide.

The procedure most frequently used and unquestionably superior to the others is that described by Guyot and Catel[9] in which phenyl-





X

---

[3] (a) Boyd and Ladhams, *J. Chem. Soc.*, 2089 (1928); (b) Blicke and Patelski, THIS JOURNAL, **58**, 273 (1936).

[4] Zincke, *Ber.*, **6**, 119 (1873); **9**, 31 (1876).

[5] Beis, *Compt. rend.*, **143**, 430 (1906).

[6] Bruhat and Thomas, *Compt. rend.*, **183**, 297 (1926).

[7] Blicke and Patelski, THIS JOURNAL, **58**, 559 (1936).

[8] Clar, John and Hawran, *Ber.*, **62**, 940 (1929).

[9] Guyot and Catel, *Compt. rend.*, **140**, 1348 (1905).

phthalide (VII) was condensed with phenylmagnesium bromide. The initial product (VIII) was transformed by hydrochloric acid or acetic acid to 1,3-diphenylisobenzofuran (IX) which, on oxidation with chromic acid, gave *o*-dibenzoylbenzene (X).

The method for preparing *o*-dibenzoylbenzene through the butadiene addition to dibenzoylethylene unquestionably is better than these just described. It has the further advantage of being readily applicable to certain substituted dibenzoylbenzenes which would be very difficult to prepare by the other methods.

Thus, by using reasonably accessible 2,3-disubstituted butadienes and substituted dibenzoylethylenes, 4,5-dialkyl or diaryl 1,2-dibenzoyl or substituted 1,2-dibenzoylbenzenes can be synthesized.

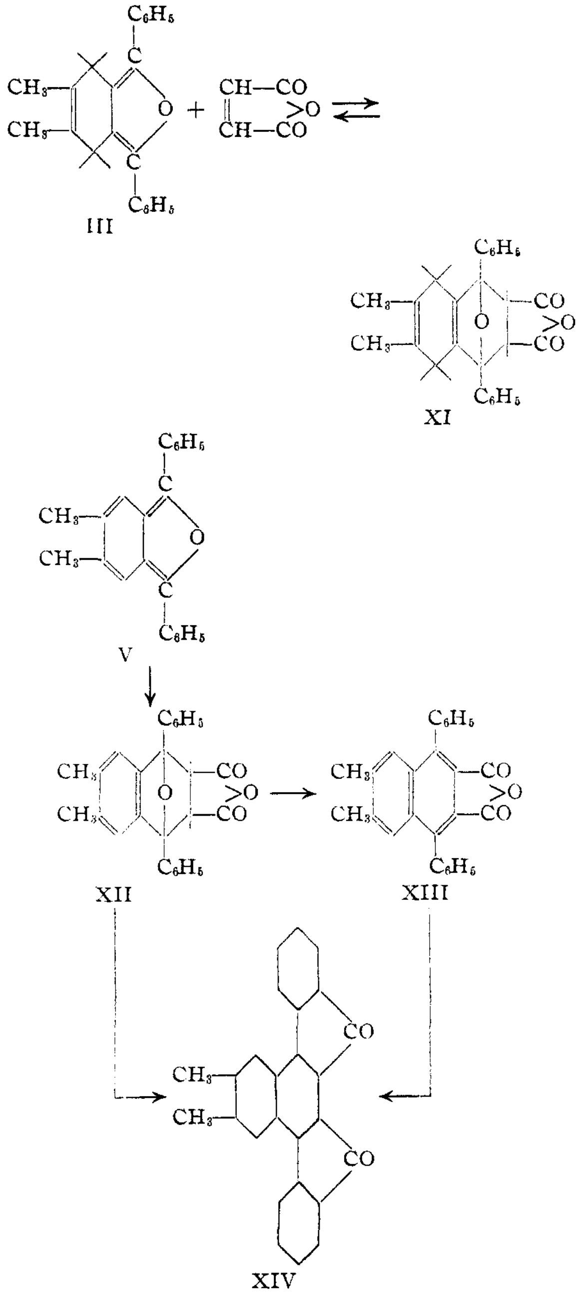
1,3-Diphenylisobenzofurans previously have been made by three processes: (1) the reduction of *o*-dibenzoylbenzenes by means of zinc and acetic acid,[3a,b] (2) the action of sulfuric acid on phthalins,[3b] (3) the action of arylmagnesium halides on aryl phthalides.[9] The unsubstituted compound has been made by the action of phenylmagnesium bromide on *o*-cyanobenzaldehyde.[3b] Since *o*-dibenzoylbenzenes can now be produced readily, the reduction of this type of compound seems the best procedure for arriving at the 1,3-diphenylisobenzofurans.

No 1,3-diphenyl-4,7-dihydroisobenzofurans (III) have been described previously.

The 1,3-diphenyl-4,7-dihydroisobenzofurans and the 1,3-diphenylisobenzofurans show marked fluorescence in dilute solution. The former are sometimes fluorescent even in the solid state. A quantitative study of the fluorescence of a series of these substances is now under way.

The isobenzofurans are useful as intermediates in various syntheses since they contain an active diene conjugated system. They add various compounds of the α,β-unsaturated carbonyl type. Thus, 1,3-diphenyl-5,6-dimethylisobenzofuran (V) is converted with maleic anhydride to 1,4-diphenyl-1,4-oxido-6,7-dimethyl-1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylic acid anhydride (XII). The dihydroisobenzofurans also contain a similar active conjugated system but the reaction with maleic anhydride is so readily reversible that isolation of pure products was not accomplished (III $\rightleftarrows$ XI).

Additions of this type (V → XII) have been described by Weiss,[10] who added ethyl cinnamate, indene, maleic anhydride and acrolein to 1,3-diphenylisobenzofuran, and maleic anhydride and acrolein to 1,3-di-α-naphthylisobenzofuran.



Barnett[11] added maleic anhydride and *p*-benzoquinone to 1,3-diphenylisobenzofuran and Dufraisse[12] *p*-benzoquinone and naphthoquinone.

---

(10) Weiss and Beller, *Monatsh.*, **61**, 143 (1932); Weiss and Abeles, *ibid.*, **61**, 162 (1932); Weiss and Kaltes, *ibid.*, **65**, 351 (1935); Weiss, *ibid.*, **71**, 6 (1937).

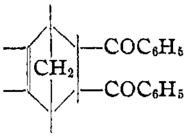
(11) Barnett, *J. Chem. Soc.*, 1326 (1935).

(12) Dufraisse and Compagnon, *Compt. rend.*, **207**, 585 (1938); Dufraisse and Priou, *Bull. soc. chim.*, [5] **5**, 502, 611 (1938).

By treatment of these adducts with hydrogen chloride, napththalene derivatives are produced and the adducts or the corresponding napthalenes are converted by sulfuric acid to 1,2,3,4-dibenzoylenenaphthalenes. Thus, the adduct (XII) is converted by hydrogen chloride to 1,4-diphenyl-6,7-dimethyl-2,3-naphthalic anhydride (XIII) and by sulfuric acid to 6,7-dimethyl-1,2,3,4-dibenzoylenenaphthalene (XIV).

Because of the ease with which many 1,3-diphenylisobenzofurans can now be made, satisfactory syntheses of 1,4-diaryl or substituted diaryl 6,7-dialkyl or diaryl 2,3-mono- or disubstituted naphthalenes are made available. A further study is being made of the scope of these preparative procedures.

When cyclopentadiene was added to *trans*-dibenzoylethylene, a compound presumably with structure XV was produced.



XV

This isomer must represent a molecule in which the benzoyl groups are *trans* or on opposite sides of the ring. A second isomer with the two benzoyl groups on the same side was obtained by addition of cyclopentadiene to *cis*-dibenzoylethylene. Neither of these adducts could be converted to furans by the procedure used for the cyclohexene derivatives.

Experimental

1,2-Dimethyl-4,5-dibenzoylcyclohexene.—To a solution of 40 g. of *trans*-dibenzoylethylene[13] in 200 cc. of absolute ethanol was added 35 g. of crude 2,3-dimethylbutadiene (unredistilled dehydration product of pinacol with 48% hydrobromic acid). The mixture was refluxed for three hours on the steam cone and allowed to cool, whereupon the product crystallized; yield 54 g. Purifications by recrystallization from 95% ethanol gave large plate-like prisms, m. p. 111–111.5° (corr.). On the first recrystallization 1.5 g. of a less soluble product remained undissolved in the hot ethanol and was identified as the corresponding dihydroisobenzofuran described in a subsequent procedure. The adduct gives a lemon yellow color in concentrated sulfuric acid.

Anal. Calcd. for $C_{22}H_{22}O_2$: C, 83.02; H, 6.92. Found: C, 82.92; H, 7.05.

cis-Dibenzoylethylene gives the same 2,3-dimethylbutadiene adduct.

Anal. Calcd. for $C_{22}H_{22}O_2$: C, 83.02; H, 6.92. Found: C, 82.92; H, 7.05.

1,2-Dimethyl-4,5-dibenzoylcyclohexene Monodinitrophenylhydrazone.—The product separated from an ethanol solution of the reactants after standing overnight: orange crystals from ethanol; m. p. 226–228° (corr.) with decomposition.

Anal. Calcd. for $C_{28}H_{26}O_5N_4$: N, 11.25. Found: N, 11.20.

1,2 - Dimethyl - 1,2 - dibromo - 4,5 - dibenzoylcyclohexane.—The addition product was prepared in glacial acetic acid: small white crystals from ethanol or petroleum ether (b. p. 60–110°); m. p. 170–171° (corr.) with decomposition.

Anal. Calcd. for $C_{22}H_{22}O_2Br_2$: C, 55.23; H, 4.60. Found: C, 55.37; H, 4.86.

1,3 - Diphenyl - 5,6 - dimethyl - 4,7 - dihydroisobenzofuran.—To a nearly boiling solution of 5 g. of 1,2-dimethyl-4,5-dibenzoylcyclohexene in 75 cc. of acetic anhydride was added a few drops of sirupy phosphoric acid. The mixture was allowed to reflux for ten minutes, although the product started to come out after the first minute or two. After cooling the solution, the product was filtered, washed with water and recrystallized from benzene: yellowish-green fluorescent crystals, m. p. 225–226° (corr.); yield 4.7 g. (99%).

Anal. Calcd. for $C_{22}H_{20}O$: C, 88.00; H, 6.67. Found: C, 87.82; H, 6.79.

The furan exhibited a blue fluorescence in solution in organic solvents. With concentrated sulfuric acid, it gives an orange-brown color.

1,2-Dimethyl-4,5-dibenzoylbenzene.—A solution of 5 cc. of bromine in 30 cc. of glacial acetic acid was added slowly to a boiling suspension of 15 g. of 1,3-diphenyl-5,6-dimethyl-4,7-dihydroisobenzofuran in 200 cc. of acetic acid, 30 g. of sodium acetate and 15 cc. of water. Within a few minutes the bromine was completely absorbed and all of the furan dissolved. Reflux was continued for five minutes and then the solution was poured directly into 500–600 cc. of hot water, after which it was allowed to cool slowly for several hours. The product was filtered, dissolved in 300 cc. of ethanol and decolorized with norit: small white rectangular plates from ethanol, m. p. 143–144° (corr.); yield 14.2 g. (90%). The product gave a violet color in concentrated sulfuric acid.

Anal. Calcd. for $C_{22}H_{18}O_2$: C, 84.07; H, 5.73. Found: C, 83.81; H, 5.93.

2-Methyl-4,5-dibenzoylbenzoic Acid.—To a mixture of 25 cc. of pyridine, 35 cc. of water, 5 g. of potassium permanganate and 1 cc. of 10% aqueous sodium hydroxide was added 2 g. of 1,2-dimethyl-4,5-dibenzoylbenzene. The solution was refluxed for thirty minutes after which time all the permanganate was reduced. The solution was cooled, acidified with sulfuric acid and the manganese dioxide reduced with sodium bisulfite. The white precipitate was filtered, dissolved in 50 cc. of 5% aqueous sodium hydroxide, again filtered and reprecipitated with dilute sulfuric acid. The product was purified by recrystallization from benzene: small white crystals, m. p. 196–197° (corr.); yield 1.4 g. (64%).

Anal. Calcd. for $C_{22}H_{16}O_4$: C, 76.74; H, 4.65; neut. equiv., 344. Found: C, 76.50; H, 4.77; neut. equiv., 340.

---

[13] Lutz, THIS JOURNAL, **52**, 3434 (1930).

1,3-Diphenyl-5,6-dimethylisobenzofuran.—A mixture of 3 g. of 1,2-dimethyl-4,5-dibenzoylbenzene, 3 g. of sodium hydroxide and 75 cc. of 95% ethanol was refluxed until the solution had turned dark brownish-red in color (usually about forty-five minutes). Then 3 g. of active zinc dust (prepared by suspending zinc dust in dilute hydrochloric acid, stirring well for one minute, decanting and washing with water until free of acid) was added and refluxing continued until the red solution became light yellow (usually five to forty-five minutes, depending on the activity of the zinc dust). The reaction should be discontinued as soon as the yellow color has appeared, otherwise the reduction proceeds too far. The hot solution was next filtered and poured into 70 cc. of glacial acetic acid and stirred to help precipitation. Within half a minute, the furan started to come out of solution. About 10 cc. of water was then added to ensure complete precipitation and the mixture was digested for about five minutes on the hot plate before allowing to cool. The product was purified from benzene or acetone: orange-yellow needles, m. p. 187–188° (corr.); yield 2.8 g. (97%).

Anal. Calcd. for $C_{22}H_{18}O$: C, 88.58; H, 6.04. Found: C, 88.13; H, 6.01.

The product exhibited a brilliant blue-green fluorescence in solution in organic solvents. It gave a reddish-orange color in concentrated sulfuric acid.

When an ethanolic solution of the benzofuran was illuminated by a strong lamp for a few days, it was reconverted completely to the 1,2-dimethyl-4,5-dibenzoylbenzene.[14]

A second procedure for preparing 1,3-diphenyl-5,6-dimethylisobenzofuran is from 1,3-diphenyl-5,6-dimethyl-5,6-dibromo-4,5,6,7-tetrahydroisobenzofuran. A solution of 1 g. of the dibromo compound in 30 cc. of glacial acetic acid and 10 cc. of acetic anhydride was heated nearly to boiling, then 8 g. of anhydrous sodium acetate and 10 cc. of glacial acetic acid was added, and the mixture refluxed for one-half hour. Upon cooling, the 1,3-diphenyl-5,6-dimethylisobenzofuran separated as yellow needles; yield 0.3 g. The mother liquor was then heated nearly to boiling and water was added until just turbid. Upon cooling, 0.36 g. of 1,2-dimethyl-4,5-dibenzoylbenzene precipitated.

1,3 - Diphenyl - 5,6 - dibromo - 5,6 - dimethyl - 4,5,6,7-tetrahydroisobenzofuran.—To a solution of 1 g. of 1,3-diphenyl-5,6-dimethyl-4,7-dihydroisobenzofuran in 80 cc. of chloroform was added a solution of 0.17 cc. of bromine in 15 cc. of chloroform over a period of ten minutes. The resulting solution was then evaporated to about 10 cc. and 5 cc. of petroleum ether (b. p. 60–110°) was added. The immediate precipitate consisting of unchanged dihydroisobenzofuran was filtered and the solution concentrated until the dibromo derivative crystallized. It was purified by recrystallization from ethanol: small light yellow crystals, m. p. 155–156° (corr.) with decomposition; yield 0.58 g. (38%; 60% based on unrecovered dihydroisobenzofuran).

Anal. Calcd. for $C_{22}H_{20}OBr_2$: C, 57.39; H, 4.35. Found: C, 57.76; H, 4.68.

1,4 - Diphenyl - 1,4 - oxido - 6,7 - dimethyl - 1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylic Anhydride.—To a solution of 1.5 g. of 1,3-diphenyl-5,6-dimethylisobenzofuran in 75 cc. of benzene was added 0.5 g. of powdered maleic anhydride. Upon the addition of the anhydride there was a brilliant flash of red color which immediately disappeared, leaving a colorless solution which no longer fluoresced. The product soon separated. Purified from toluene, it gave tiny white crystals, m. p. (sealed tube) 254–255° (corr.) with decomposition; yield 2 g. (quant.).

Anal. Calcd. for $C_{26}H_{20}O_4$: C, 78.78; H, 5.05. Found: C, 78.65; H, 5.38.

The product gave a lemon yellow color in concentrated sulfuric acid.

1,4-Diphenyl-6,7-dimethyl-2,3-naphthalic Anhydride.—A suspension of 2 g. of the oxido compound in 150 cc. of absolute methanol was saturated with dry hydrogen chloride and then refluxed for two hours, while a slow stream of the hydrogen chloride was kept continuously bubbling through the reaction mixture. The oxido compound rapidly dissolved and the solution exhibited a faint fluorescence. After evaporation to dryness, 25 cc. of water, 5 g. of sodium hydroxide and 100 cc. of ethanol were added and the mixture refluxed for four hours. The solution was then cooled and acidified to congo red. The resulting white precipitate was filtered and dissolved in 10% aqueous sodium hydroxide, filtered and reprecipitated with acid. Upon purification by recrystallization from benzene, it gave tiny white crystals, m. p. 324–325° (corr.) with decomposition and some sublimation; yield 1.3 g. (68%).

Anal. Calcd. for $C_{26}H_{18}O_3$: C, 82.80; H, 4.76. Found: C, 83.06; H, 4.85.

The product gave a greenish-yellow color in concentrated sulfuric acid.

6,7-Dimethyl-1,2,3,4-dibenzoylenenaphthalene.—A mixture of 10 cc. of concentrated sulfuric acid and 0.5 g. of 1,4 - diphenyl - 1,4 - oxido - 6,7 - dimethyl - 1,2,3,4 - tetrahydronaphthalene-2,3-dicarboxylic anhydride was allowed to stand for three and one-half hours. After this time the solution, which had turned from a light yellow to a deep green, was poured over 30 g. of ice. The red precipitate was purified by recrystallization from boiling acetic acid: tiny red needles, m. p. >325°; yield 0.2 g.

Anal. Calcd. for $C_{26}H_{16}O_2$: C, 86.67; H, 4.44. Found: C, 86.58; H, 4.56.

4,5-Dibenzoylcyclohexene.—To a cooled solution of 15 g. (1.5 moles) of butadiene in 200 cc. of benzene was added 40 g. of *trans*-dibenzoylethylene. The mixture was heated in a pressure bomb for two hours at 100°. The benzene was evaporated to 75 cc. and 125 cc. of methanol was added. Upon cooling, the product separated. It was purified by crystallization from ethanol: fine white crystals, m. p. 111.5–112° (corr.); yield 49 g. (quant.).

Anal. Calcd. for $C_{20}H_{18}O_2$: C, 82.75; H, 6.21. Found: C, 82.81; H, 6.47.

1,2-Dibromo-4,5-dibenzoylcyclohexane.—The procedure used was the same as for the bromination of the dimethyl homolog. The product was obtained in 90% yield and was purified from petroleum ether (b. p. 60–110°): small white crystals, m. p. 148–149° (corr.).

Anal. Calcd. for $C_{20}H_{18}O_2Br_2$: C, 53.33; H, 4.00. Found: C, 53.61; H, 4.22.

---

[14] Guyot and Catel, *Bull. soc. chim.*, [3] **35**, 1127 (1906).

1,3-Diphenyl-4,7-dihydroisobenzofuran.—The procedure used was that employed for preparation of the dimethyl compound: yellowish-green crystals from petroleum ether (b. p. 60–110°), m. p. 120–121° (corr.); yield 99%.

Anal. Calcd. for $C_{20}H_{16}O$: C, 88.23; H, 5.88. Found: C, 88.04; H, 6.28.

1,3 - Diphenyl - 5,6 - dibromo - 4,5,6,7 - tetrahydroisobenzofuran.—To a solution of 4 g. of 1,3-diphenyl-4,7-dihydroisobenzofuran in 30 cc. of glacial acetic acid was added dropwise a solution of 0.76 cc. of bromine in 10 cc. of acetic acid. The mixture was cooled and 4 g. (67%) of product separated. It was purified by crystallization from petroleum ether (b. p. 60–110°): yellow crystals, m. p. 150–151° (corr.) with decomposition.

Anal. Calcd. for $C_{20}H_{16}OBr_2$: C, 55.55; H, 3.72. Found: C, 55.01; H, 3.77.

This compound is relatively unstable and consequently difficult to obtain in an absolutely pure state. For this reason, the analysis does not agree with the theoretical as closely as is usually expected.

***o*-Dibenzoylbenzene.**—This was prepared in the same manner as the 4,5-dimethyl derivative; yield 85%. It was purified by recrystallization from ethanol or petroleum ether (b. p. 60–110°): white crystals, m. p. 145–146° (corr.); previously reported melting points are Zincke,[4] 145–146°; Beis,[5] 149°; Bruhat and Thomas,[6] 148°; Boyd and Ladhams,[3a] 145°.

1,3-Diphenylisobenzofuran.—This was prepared in the same manner as the dimethyl homolog. After the zinc dust reduction of 1 g. of dibenzoylbenzene, the filtered solution was treated with 5 cc. of concentrated hydrochloric acid with stirring. In a few seconds, the product separated in the form of yellow flakes. The product was purified by crystallization from petroleum ether (b. p. 60–110°): yellow crystals, m. p. 125–126° (corr.); yield 69%; previously reported melting points, Guyot and Catel,[9] 125°; Boyd and Ladhams,[3a] 120–125°.

Addition of Maleic Anhydride to 1,3-Diphenyl-4,7-dihydroisobenzofuran and to 1,3-Diphenyl-5,6-dimethyl-4,7-dihydroisobenzofuran.—These addition reactions were carried out in benzene solution. Mixing of the reactants was followed immediately by formation of an orange-red color which slowly faded. The characterisric fluorescence of the furans disappeared after refluxing for a short time. By concentration of the solvent products crystallized which, however, could not be purified owing to reversal to the furan and maleic anhydride.

2,3 - Dibenzoyl - 1,4 - endomethylene - 1,2,3,4 - tetrahydrobenzene.—To a solution of 10 g. of *trans*-dibenzoylethylene in 45 cc. of dry benzene was added 10 g. of cyclopentadiene. Heat was evolved and the yellow color faded. The mixture was refluxed for several hours, then well cooled, whereupon an oil separated. Concentration to a small volume, addition of ethanol, scratching and cooling resulted in the formation of crystals. These were purified by recrystallization from methanol: white crystals, m. p. 78–79° (corr.); yield 11 g. (89%).

Anal. Calcd. for $C_{21}H_{18}O_2$: C, 83.11; H, 5.96. Found: C, 83.00; H, 6.15.

A solution of 0.5 g. of *cis*-dibenzoylethylene in 15 cc. of absolute ethanol was refluxed with 1 g. of cyclopentadiene for four hours. This gave white needles on cooling. Purified by recrystallization from ethanol, m. p. 160–161° (corr.). This compound was a second isomer.

Anal. Calcd. for $C_{21}H_{18}O_2$: C, 83.11; H, 5.96. Found: C, 82.70; H, 6.12.

Summary

New and unusually satisfactory methods for preparing dihydroisobenzofurans, isobenzofurans and *o*-dibenzoylbenzenes are described.

Butadiene and 2,3-dimethylbutadiene have been condensed with *trans*-dibenzoylethylene to give 4,5-dibenzoylcyclohexene and its 1,2-dimethyl derivative. These dibenzoyl compounds are quantitatively converted by means of a little phosphoric acid in acetic anhydride to dihydroisobenzofurans. These, in turn, by bromine and sodium acetate give excellent yields of *o*-dibenzoylbenzenes.

It has been shown that the *o*-dibenzoylbenzenes can be converted quantitatively to isobenzofurans by ethanolic sodium hydroxide and activated zinc dust.

Both the dihydroisobenzofurans and the isobenzofurans add maleic anhydride and the adducts of the latter may be converted to naphthalene derivatives.

Cyclopentadiene also adds to *trans*- and *cis*-dibenzoylethylenes with formation of isomeric adducts.

URBANA, ILLINOIS RECEIVED NOVEMBER 10, 1939