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

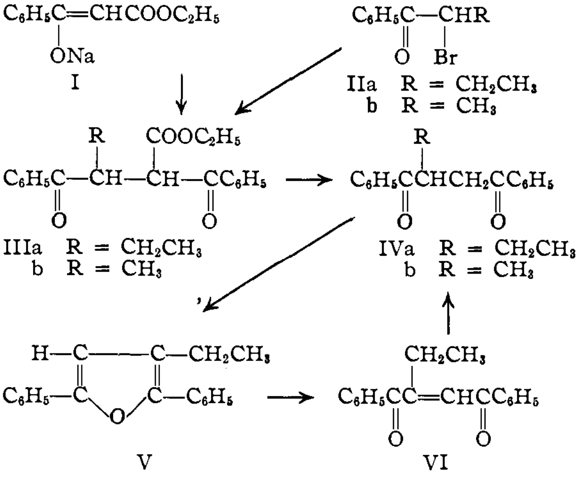
# The Syntheses of 1,2-Dibenzoylbutane and 1,2-Dibenzoyl-1-butene and the Reaction of 1,2-Dibenzoyl-1-butene with Morpholine[1,2]

BY PHILIP S. BAILEY AND WAFAI WAHID HAKKI[3]

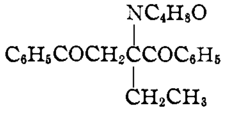
In earlier papers it has been shown that 1,2-dibenzoyl-1-propene[4] and 2,3-dibenzoyl-1-N-morpholinyl-2-butene[5] react with morpholine in a surprising fashion to form 1,2-dibenzoyl-3-N-morpholinylpropane and 2,3-dibenzoyl-1,4-di-(N-morpholinyl)-butane respectively. The present paper deals with the preparation of a homolog of 1,2-dibenzoyl-1-propene, namely, 1,2-dibenzoyl-1-butene (VI), and the study of its reaction with morpholine as a test of the generality of this interesting reaction of 1,2-dibenzoyl-1-alkenes with amines.

In the synthesis of 1,2-dibenzoyl-1-butene (VI), 1,2-dibenzoylbutane (IVa) was first made by the method which Kapf and Paal[6] used to synthesize 1,2-dibenzoylethane, after which IVa was converted to VI through the corresponding furan (V). The synthesis of IVa consisted of the reaction of sodio ethyl benzoylacetate (I) with α-bromobutyrophenone (IIa) to form IIIa which was hydrolyzed and decarboxylated to IVa. Lauer and Spielman[7] have also used this type of synthesis in the preparation of 1,2-dibenzoylpropane (IVb), but neglected to report experimental details. Their work was repeated as a part of the study of this synthetic method. A great improvement in yield over that reported by Kapf and Paal[6] in their synthesis of 1,2-dibenzoylethane was obtained in our synthesis of 1,2-dibenzoylbutane. The principal difference in procedure was in the use of a much shorter time period in the hydrolysis of the carbethoxy derivative (IIIa). Kapf and Paal[6] obtained a crystalline carbethoxy derivative. In our synthesis of 1,2-dibenzoylpropane (IVb) a crystalline carbethoxy derivative (IIIb) was obtained and characterized, but in our synthesis of 1,2-dibenzoylbutane (IVa) the intermediate IIIa would not crystallize.

3-Ethyl-2,5-diphenylfuran (V), prepared by the furanization of IVa, could not be crystallized. The oily furan gave no refractive index; it gave a "Tyndall Effect" even after careful distillation. A possible explanation of these phenomena is that associated furan molecules are colloidally dispersed through the monomer.[8] The characteristic nitric acid oxidation[9] of the furan (V) gave 1,2-dibenzoyl-1-butene (VI), the structure of which was demonstrated by reduction to IVa using zinc and acetic acid.

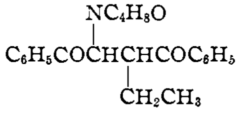


The butene (VI) reacted with morpholine, but not as readily nor in as good yield as did 1,2-dibenzoyl-1-propene.[4] In order to distinguish among the at least three possible structures for the addition compound (VII, VIII or IX), the substance was first treated with reagents which bring about furanization where possible. Cyclization did occur, narrowing down the possible structures for the addition compound to VIII and IX. The characteristic nitric acid oxidation of the furan (X or XI) gave the ethylene derivative.



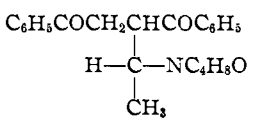
$C_6H_5COCH_2\overset{NC_4H_8O}{\underset{CH_2CH_3}{C}}COC_6H_5$

VII



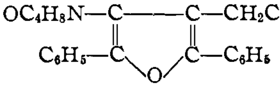
$C_6H_5CO\overset{NC_4H_8O}{CH}\underset{CH_2CH_3}{CH}COC_6H_5$

VIII

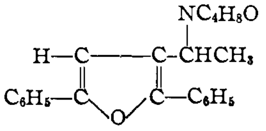


$C_6H_5COCH_2\underset{H-\underset{CH_3}{C}-NC_4H_8O}{CH}COC_6H_5$

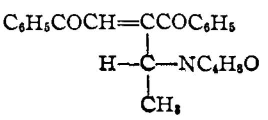
IX



X



XI



$C_6H_5COCH{=}\underset{H-\underset{CH_3}{C}-NC_4H_8O}{C}COC_6H_5$

XII

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[1] From the M.A. Thesis of W. W. Hakki, January, 1949.

[2] This work was supported in part by a Frederick Gardner Cottrell grant from the Research Corporation, New York, N. Y.

[3] Holder of a Syrian Government Scholarship.

[4] Lutz and Bailey, THIS JOURNAL, **67**, 2229 (1945).

[5] Bailey and Nowlin, *ibid.*, **71**, 732 (1949).

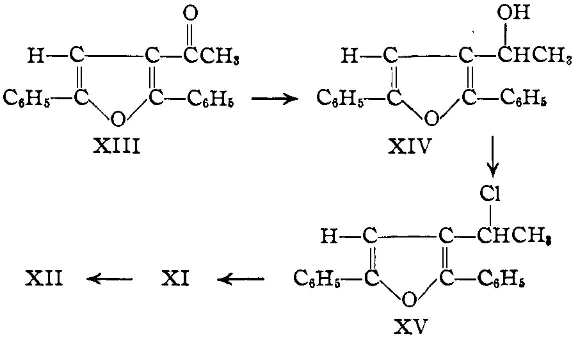
[6] Kapf and Paal, *Ber.*, **21**, 1487, 3056 (1888).

[7] Lauer and Spielman, THIS JOURNAL, **55**, 4928 (1933).

[8] The authors are indebted to Professor Norman Hackerman of this department for this suggestion.

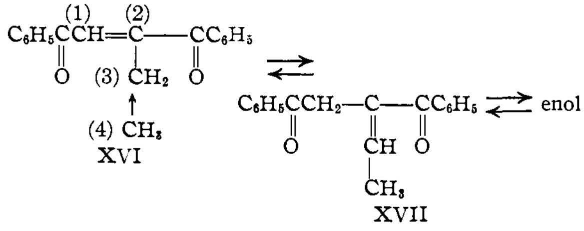
[9] Lutz and Wilder, THIS JOURNAL, **56**, 978 (1934).

The furan was shown to be XI by synthesis from known 3-acetyl-2,5-diphenylfuran (XIII),[10] thus establishing the structure of the addition compound as IX and the structure of the ethylenic derivative of the furan as XII. The synthesis involved reduction of XIII to XIV by the Meerwein–Ponndorf–Verley method,[11] using aluminum isopropoxide, followed by conversion of XIV to XV by means of ethereal hydrogen chloride solution. The chloroethyl compound (XV), upon treatment with morpholine, gave XI, which was shown to be identical with the furan formed from the addition product of VI and morpholine.



Earlier, an attempt to synthesize XI from 3-chloro-2,5-diphenylfuran by means of a chloroethylation reaction, followed by treatment with morpholine and hydrogenolysis of the 3-chloro group, failed in the first step. Also an attempt to synthesize X from 3-morpholinyl-2,5-diphenylfuran by chloroethylation followed by hydrogenolysis of the chloro group failed in the chloroethylation step. Chloroethylations have been carried out with anisole[12] in the benzene series, and bromo- and chloromethylations take place with ease in the diphenylfuran series.[13,5] However, it appears that the chloroethylation reaction in the *beta* position of phenylated furans is not practical.

A mechanism to account for the reaction of amines with 1,2-dibenzoyl-1-alkenes has been suggested in an earlier paper[4]. As applied to the present case, intermediate XVII is suggested. The amine adds to this to give IX:



The fact that 1,2-dibenzoyl-1-butene (XVI) reacts less readily with morpholine than does 1,2-dibenzoyl-1-propene[4] is in line with this mechanism. The electron releasing effect of the methyl group (carbon 4 in XVI) would tend to decrease the mobility of the hydrogens on the adjacent methylene group (carbon 3).

It was reported in an earlier paper[4] that *trans*-1,2-dibenzoyl-1-propene was converted to the *cis* isomer by treatment with triethylamine and that the *cis* isomer was stable under these conditions. When VI, which should have the *cis* configuration due to its method of preparation,[9] was treated in this manner a reaction occurred giving a non-crystalline substance which was not identified. It was also reported earlier that 1,2-dibenzoyl-3-morpholinyl-1-propene underwent a rearrangement spontaneously over a period of time, or in an hour's time when heated at its melting point; the product was 4-benzoyl-2-phenylfuran.[14] 1,2-Dibenzoyl-3-morpholinyl-1-butene (XII) was found to decompose slowly at room temperature or within thirty minutes at its melting point with the elimination of morpholine; however, no crystalline product could be isolated.

The morpholinylethylfuran (XI) was found to be surprisingly stable to hot acids, whereas the saturated diketone (IX) was found to be deaminated under these conditions, as would be expected. No crystalline product could be isolated, however.

## Experimental[15]

**α-Bromobutyrophenone** (IIa) was made by the dropwise addition of a solution of 160 g. (1 mole) of bromine and 250 ml. of dry ether to a stirred solution of 148 g. (1 mole) of butyrophenone in 600 ml. of dry ether. Evaporation left the straw-colored, oily α-bromobutyrophenone which was used as such in the next step.

**1,2-Dibenzoylbutane** (IVa). (a) **1,2-Dibenzoyl-1-carbethoxybutane** (IIIa).—To 500 ml. of an ethanolic solution of sodium ethoxide (prepared from 23 g. or 1 gram atom of sodium) was added, dropwise with stirring, 192 g. (1 mole) of ethyl benzoylacetate. Next was added the crude α-bromobutyrophenone described in the preceding experiment, with stirring, over a period of one hour. Stirring was continued for three hours. The mixture was filtered (75 g. of sodium bromide obtained) and the filtrate was evaporated, leaving an oily residue which was carefully washed with water. All attempts to crystallize the residue (340 g.) failed.

(b) **Hydrolysis and Decarboxylation.**—To a solution of the crude carbethoxy compound (IIIa) in 200 ml. of alcohol was added 1125 ml. of an approximately 8% aqueous solution of sodium hydroxide (90 g. or 2.25 moles). The mixture was stirred vigorously for four hours after which time it was cooled. Filtration yielded a colorless solid which weighed 180 g. after it had been washed and dried; recrystallized from ethanol, m. p. 59–60°, 68% yield from ethyl benzoylacetate.

*Anal.* Calcd. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.41; H, 7.11.

When the hydrolysis was carried out over periods of twenty-four hours and eight days, the yields were 33 and 15%, respectively. Kapf and Paal,[6] in their synthesis of 1,2-dibenzoylethane, used an eight day hydrolysis

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[10] Lutz and Rowlett, THIS JOURNAL, **70**, 1359 (1948).

[11] See Wilds in Adams, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 198.

[12] Quelet, *Bull. soc. chim.*, [5] **7**, 199 (1940).

[13] Lutz and Bailey, THIS JOURNAL, **68**, 2002 (1946).

[14] Bailey and Lutz, THIS JOURNAL, **67**, 2232 (1945).

[15] All melting points are corrected. A few of the microanalyses were carried out by the Clark Microanalytical Laboratory, Urbana, Illinois.

period. In the absence of ethanol, hydrolysis with 5% aqueous sodium hydroxide gave benzoic acid as the only isolable crystalline product.

**1,2-Dibenzoylpropane (IVb).** (a) **1,2-Dibenzoyl-1-carbethoxypropane (IIIb).**—α-Bromopropiophenone (IIb) was made and allowed to react with sodio ethyl benzoylacetate (I) using the procedure described in the preparations of IIa and IIIa. Unlike the carbethoxybutane (IIIa), the carbethoxypropane (IIIb) crystallized from the ethanol solution when the volume was reduced by one-half and the mixture was cooled. The crystals were collected and washed free of sodium bromide. The yield was 22.5% and the melting point was 98–103°. Several recrystallizations from ethanol raised the melting point to 104–105°.

*Anal.* Calcd. for $C_{20}H_{20}O_4$: C, 74.05; H, 6.22. Found: C, 73.88; H, 6.43.

(b) **Hydrolysis and decarboxylation** was carried out by the same method used in the preparation of IVa with the exception that the eight-day period prescribed by Kapf and Paal[6] was used. The yield of 1,2-dibenzoylpropane (IVb) from IIIb was 92% and the melting point was 102–104°. The material was identified by a mixture melting point with a known sample.[16]

**3-Ethyl-2,5-diphenylfuran (V).**—To a refluxing solution of 500 ml. of glacial acetic acid, 400 ml. of concentrated hydrochloric acid and 260 g. of stannous chloride was added a solution of 70 g. of 1,2-dibenzoylbutane (IVa) in 200 ml. of glacial acetic acid. Heating was continued for five minutes after which the reaction mixture was poured into 1400 ml. of water. The aqueous mixture was extracted with ether and the ether extract was washed, dried and evaporated. Fifty-five grams of an oil was left which resisted crystallization. It was purified by two distillations under reduced pressure (132–136° at 0.1 mm.).

*Anal.* Calcd. for $C_{18}H_{16}O$: C, 87.06; H, 6.49. Found: C, 86.72; H, 6.42.

A refractive index could not be obtained for the furan. No line of division could be found in the field of the refractometer. The liquid gave a clear "Tyndall Effect"; the beam of light passing through the liquid had clear boundaries and was cloudy in appearance.

**1,2-Dibenzoyl-1-butene (VI).**—A suspension of 25.5 g. of 3-ethyl-2,5-diphenylfuran (V) in 200 ml. of glacial acetic acid was treated with a solution of 20 ml. of nitric acid and 125 ml. of glacial acetic acid. Oxides of nitrogen were evolved. After twenty minutes the resulting solution was poured into cold water, whereupon a yellow solid precipitated. Filtration yielded 19 g. (74% yield) of material which became colorless and melted at 92–94° after several recrystallizations from ethanol. It decolorized a dilute acetone solution of potassium permanganate.

*Anal.* Calcd. for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.65; H, 6.09.

**Reduction of 1,2-Dibenzoyl-1-butene (VI) to 1,2-dibenzoylbutane (IVa)** was accomplished by adding a spatula full of zinc dust to a solution of 1 g. of VI in 10 ml. of glacial acetic acid, and warming the mixture on a steam-bath for twenty minutes. The zinc was filtered off and the filtrate was diluted with cold water, giving a mixture from which a solid crystallized after five hours cooling. The crystals were separated and recrystallized from ethanol; m. p. 59–60°, no depression in a mixture melting point with known 1,2-dibenzoylbutane (IVa).

**The Addition of Morpholine to 1,2-Dibenzoyl-1-butene (VI).**—A solution of 20 g. of VI and 90 ml. of morpholine was kept at room temperature for twelve hours. The solution was then diluted with 250 ml. of benzene, washed with water several times and evaporated. Crystallization of the residue from ethanol gave 18 g. (64% yield) of material which melted at 120–122° after several recrystallizations from ethanol. Nothing crystalline was obtained when the reaction was carried out in isopropyl ether solution at 50–60°; only a 25% yield was obtained in ether at room temperature.

*Anal.* Calcd. for $C_{22}H_{25}NO_3$: C, 75.18; H, 7.17. Found: C, 75.42; H, 7.24.

When the addition compound was treated with refluxing glacial acetic acid for fifteen minutes, an oily material was obtained which was insoluble in acids. It completely resisted crystallization efforts.

**Conversion of the Addition Product (IX) to 3-(1′-N-morpholinylethyl)-2,5-diphenylfuran (XI).**—To a solution of 5 g. of the morpholine addition compound (IX) and 50 ml. of acetyl chloride was added enough concentrated sulfuric acid to neutralize the amine (0.75 ml.), followed by twenty drops excess. The solution turned pale green. After twenty minutes the mixture was poured into cold water and was neutralized with sodium carbonate; a thick yellow oil separated and was dissolved in ether. The ether extract was washed, dried and evaporated leaving an oily residue which would not crystallize. Attempts to prepare the amine hydrochloride by adding ethereal hydrogen chloride solution to an acetone or ethereal solution of the amine produced a crystalline substance which became oily when exposed to air. The picrate of the aminofuran was made by adding an equivalent amount of picric acid in 5% ethanol solution to an absolute ethanol solution of the amine. A thick oily substance formed which crystallized when the reaction mixture was heated over a steam-bath for ten minutes. After recrystallization from a 50–50 ethanol–acetone solution the picrate melted at 174–176°. The picrate was converted back to the free amine by shaking it with 5% sodium hydroxide solution and ether until everything dissolved. The ether extract was washed, dried and evaporated, leaving 3.3 g. of an oily residue (65% yield). In another experiment the picrate was purified further by recrystallization from ethanol–acetone and analyzed (m. p. 175–177°).

*Anal.* Calcd. for $C_{28}H_{26}N_4O_9$: C, 59.78; H, 4.66. Found: C, 59.56; H, 4.82.

When the furanization was attempted in acetic acid solution at room temperature, no reaction occurred. When the temperature was raised to 45° and kept there for seven hours, a yield of 60% of the oily aminofuran (XI) was obtained. The aminofuran was stable to refluxing acetic acid for fifteen minutes and to refluxing 6 *N* hydrochloric acid for six hours. Identifications were through the picrate.

**3-(1′-N-Morpholinylethyl)-2,5-diphenylfuran (XI) from 3-Acetyl-2,5-diphenylfuran (XIII).** (a) **3-(1′-Hydroxyethyl)-2,5-diphenylfuran (XIV).**—A solution of 4 g. of 3-acetyl-2,5-diphenylfuran (XIII) (prepared by the method of Lutz and Rowlett[10]) and 80 ml. of an isopropyl alcohol solution of aluminum isopropoxide (7.5 g.) was slowly distilled over a period of two hours, using a thirteen-bulb Snyder column. Twenty milliliters of isopropyl alcohol was added during the distillation to replace that distilled over. Positive tests for acetone, using 2,4-dinitrophenylhydrazine, were obtained during the first hour of the distillation. After the reflux period, the reaction mixture was evaporated under reduced pressure and the residue was hydrolyzed with 6 *N* hydrochloric acid. The resulting mixture was extracted with ether and the ether extract was washed, dried and evaporated. Numerous attempts to crystallize the residue (3 g.) failed. It was used as such in the next step.

(b) **3-(1′-Chloroethyl)-2,5-diphenylfuran (XV).**—A solution of 3 g. of the crude hydroxyethyl compound (XIV) and 50 ml. of ethereal hydrogen chloride was set aside for forty-eight hours, after which time it was evaporated under reduced pressure. Several recrystallizations of the greenish crystalline residue from ligroin gave a pure, colorless sample (1.2 g.) which melted at 63–64°. It gave a positive Beilstein test for halogen.

*Anal.* Calcd. for $C_{18}H_{15}ClO$: C, 76.45; H, 5.35. Found: C, 76.16; H, 5.21.

(c) **Conversion to XI** was accomplished by the addition of 4 ml. of morpholine to a solution of 0.5 g. of the chloro-

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(16) Lutz and Taylor, THIS JOURNAL, **55**, 1177 (1933).

ethyl compound (XV) in 2 ml. of ether. After the reaction mixture had stood for twenty-four hours it was filtered (to remove the morpholine hydrochloride) and the filtrate was diluted with ether, washed, dried and evaporated. Treatment of the residue with an ethanolic solution of picric acid as described earlier yielded the picrate (0.2 g.) which melted at 173–175° and showed no depression in a mixture melting point with the picrate of the furan made from the product of addition of morpholine to 1,2-dibenzoyl-1-butene.

**1,2-Dibenzoyl-3-N-morpholinyl-1-butene (XII).**—To a solution of 1.6 g. of the oily morpholinylethylfuran (XI), made from the addition product (IX), in 20 ml. of glacial acetic acid was added a solution of 2 ml. of nitric acid and 10 ml. of glacial acetic acid. After twenty minutes the yellow solution was poured into water and neutralized with sodium carbonate. The mixture was extracted with ether and the ether extract was washed and evaporated. Recrystallization of the solid residue (1.3 g.) from ethanol, using *Darco*, yielded colorless crystals which melted at 113–115.5°. The substance was also obtained from the oxidation of XI made from the acetylfuran (XIII); no depression was observed in a mixture melting point of the two samples.

*Anal.* Calcd. for $C_{22}H_{23}NO_3$: C, 75.62; H, 6.64. Found: C, 75.78; H, 6.75.

The morpholinylbutene (XII) slowly decomposed on standing for several weeks. A strong odor of morpholine was noticed. No crystalline material could be isolated from the decomposition product. The same thing occurred when the compound was heated at its melting point for one-half hour.

**Treatment of 1,2-dibenzoylbutene (VI) with triethylamine** in ratio of 1 g. of VI to 10 ml. of ether and 20 ml. of triethylamine for periods of twenty-four hours or fifteen days gave an oily material when the ether and triethylamine were evaporated by a stream of air. All efforts to crystallize the oil failed.

**Attempted Chloroethylation of 3-Chloro-2,5-diphenylfuran.**—Dry hydrogen chloride was passed into a stirred solution of 25 ml. of glacial acetic acid, 0.5 ml. of paraldehyde and 1 g. of 3-chloro-2,5-diphenylfuran (m. p. 69–72°) at room temperature for eight hours. The green solution was poured into water where a dark solid settled out. The solid was separated, recrystallized from ethanol (0.6 g., m. p. 67–70°) and was identified as the chlorofuran by the mixture melting point method. When the reaction was repeated using the same materials and procedure with the exception that 0.5 g. of anhydrous zinc chloride was added and the reaction temperature was kept at 40–50° for two and one-half hours, 0.4 g. of the chlorofuran was recovered. When a comparable reaction mixture was heated at 50–60° for fifteen hours, only a brown tar was obtained. An attempted chloroethylation using Quelet's procedure[12] (1 g. of the chlorofuran, 1 ml. of paraldehyde, 20 ml. of hydrochloric acid, hydrogen chloride bubbled in for three hours) gave a recovery of 0.6 g. of the chlorofuran. It settled out from the dark reaction mixture, was collected, recrystallized and identified by the mixture melting point method.

**Attempted Chloroethylation of 3-N-Morpholinyl-2,5-diphenylfuran.**—Into a stirred solution of 1 g. of 3-N-morpholinyl-2,5-diphenylfuran (m. p. 110–114°), 1 ml. of paraldehyde and 20 ml. of glacial acetic acid was passed dry hydrogen chloride for two hours. The temperature was kept at 45° during the reaction. The mixture was poured into water, neutralized with sodium carbonate and extracted with ether. When the ether extract was washed, dried and evaporated, 0.7 g. of the morpholinylfuran was recovered (recrystallized from ethanol, m. p. 108–110°, identified by the mixture melting point method). When the reaction was attempted in aqueous medium using the procedure described for 3-chloro-2,5-diphenylfuran, a 60% recovery of the morpholinylfuran was obtained.

## Summary

1. 1,2-Dibenzoylbutane and 1,2-dibenzoylpropane have been made from ethyl benzoylacetate and the corresponding alkyl phenyl ketone by what seems to be a general method.

2. 1,2-Dibenzoyl-1-butene has been made and found to react with morpholine in a manner analogous to the reaction of 1,2-dibenzoylpropene with amines. The product was 1,2-dibenzoyl-3-N-morpholinylbutane.

3. Attempted chloroethylations of 3-chloro-2,-5-diphenylfuran and 3-morpholinyl-2,5-diphenylfuran failed.

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[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA AND SWARTHMORE COLLEGE]

# The Ultraviolet Absorption Spectra of Organic Sulfur Compounds. III. Substituted Phenyl Sulfides

BY EDWARD A. FEHNEL[1] AND MARVIN CARMACK

Considerations based on the ultraviolet absorption spectra of numerous organic compounds containing the sulfide and sulfone functions have led to the conclusion that structures in which sulfur has an expanded valence shell make important contributions to the resonance in the activated states of certain polyfunctional sulfur compounds.[2,3] The question has arisen,[2] however, as to the relative importance of contributions from such structures among the phenyl sulfides, where the strong donor properties of the sulfur atom might be expected to predominate over, if not to eliminate entirely, any tendency to withdraw electrons from the aromatic nucleus. Steric factors affecting the resonance within the phenylmercapto group must also be considered in any attempt to interpret the spectra of the phenyl sulfides. The present investigation of the absorption spectra of a number of nuclearly substituted phenyl sulfides was undertaken to provide additional data on this aspect of the problem.

## Discussion of Results

The absorption spectra of a homologous series of unsubstituted phenyl alkyl sulfides have been

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[2] Fehnel and Carmack, THIS JOURNAL, **71**, 84 (1949).

[3] Fehnel and Carmack, *ibid.*, **71**, 231 (1949).