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.

AUSTIN, TEXAS RECEIVED FEBRUARY 21, 1949

[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).

described in an earlier paper in this series.[2] The progressive modification of the spectra of these sulfides as the α-hydrogen atoms are successively replaced by methyl groups is particularly striking when the data are plotted on a linear (ε) basis, as in Fig. 1.

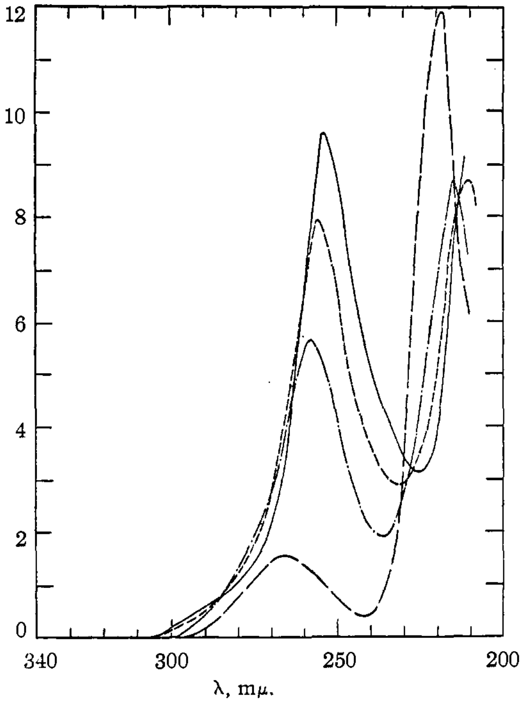
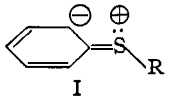
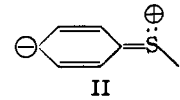


Fig. 1.—Absorption spectra of $C_6H_5SCH_3$, —; $C_6H_5SCH_2CH_3$, -----; $C_6H_5SCH(CH_3)_2$, —·—·—; and $C_6H_5SC(CH_3)_3$, — — —; solvent, ethanol.

That this is a steric effect is clearly indicated by a comparison of the curves for phenyl methyl sulfide and phenyl *t*-butyl sulfide with those for *p*-tolyl methyl sulfide and mesityl methyl sulfide (Fig. 2). The introduction of a methyl group into the para position of the phenyl methyl sulfide molecule produces the expected slight shift toward longer wave lengths (Δλ *ca.* 2–5 mμ) without changing the characteristic shape of the absorption curve. The introduction of two additional methyl groups in the ortho positions, as in mesityl methyl sulfide, however, brings about a considerable modification in the absorption, characterized particularly by a marked decrease in absorption in the 240–260 mμ region, and the resultant curve closely resembles that of phenyl *t*-butyl sulfide. Similar effects have been encountered in the spectra of many types of ortho-substituted aromatic compounds,[4,5,6,7] and have been attributed to the inhibition of resonance by steric interference with the required coplanar configuration of the molecule. The bulky *t*-butyl group in phenyl *t*-butyl sulfide is presumably capable of imposing a similar restriction on the rotation of the alkylmercapto substituent, thereby reducing the resonance contributions from forms in which the sulfur atom behaves as an electron donor with respect to the benzene ring (I, II).

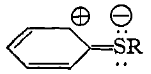


I

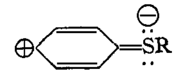


II

Although it is not known what effect steric influences might have upon resonance involving 5-covalent sulfur, there is reason to believe that the coplanarity required for resonance in tetracovalent systems may not be a prerequisite for resonance in pentacovalent systems.[8] The fact that the primary bands[9] in the spectra of phenyl *t*-butyl sulfide and mesityl methyl sulfide appear at appreciably longer wave lengths (Δλ 14 mμ and 8 mμ, respectively) than in the spectra of the parent hydrocarbons (benzene, $\lambda_{pri.}$ 204 mμ[10]; mesitylene, $\lambda_{pri.}$ 215 mμ[7]) might be interpreted as evidence for some polarization of the phenylmercapto group in the opposite direction, as in structures III and IV.[11]



III



IV

Substitution of a hydroxyl group in the para position of phenyl methyl sulfide (Fig. 3) has almost no effect on the location of the first primary band maximum (Δλ 2 mμ), although the secondary band indicated by the shoulder in the region 280–300 mμ (λ_{max} 286 mμ) is much more prominent in the spectrum of *p*-hydroxyphenyl methyl sulfide than in that of the unsubstituted sulfide ($\lambda_{infl.}$ 275 mμ[2]). The spectrum of the *p*-hydroxy derivative is further characterized by the development of a second primary band at short wave lengths ($_{max.}$ 229 mμ). When *p*-hydroxyphenyl methyl sulfide is examined in alkaline solution, a general displacement of the absorption curve toward longer wave lengths and higher intensities is observed. The second primary band seems to be absent in the spectrum of the anion, but it is possible that this may result from coalescence of this band with the first primary band.

The substitution of a hydroxyl group in the ortho position of phenyl methyl sulfide is characterized by the appearance of a well-formed peak with a maximum at 289 mμ (Fig. 3). This marked increase in the long wave length absorp-

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(4) Remington, THIS JOURNAL, **67**, 1838 (1945), and refs.

(5) Jones, *ibid.*, **67**, 2127 (1945).

(6) Brown and Reagan, *ibid.*, **69**, 1032 (1947).

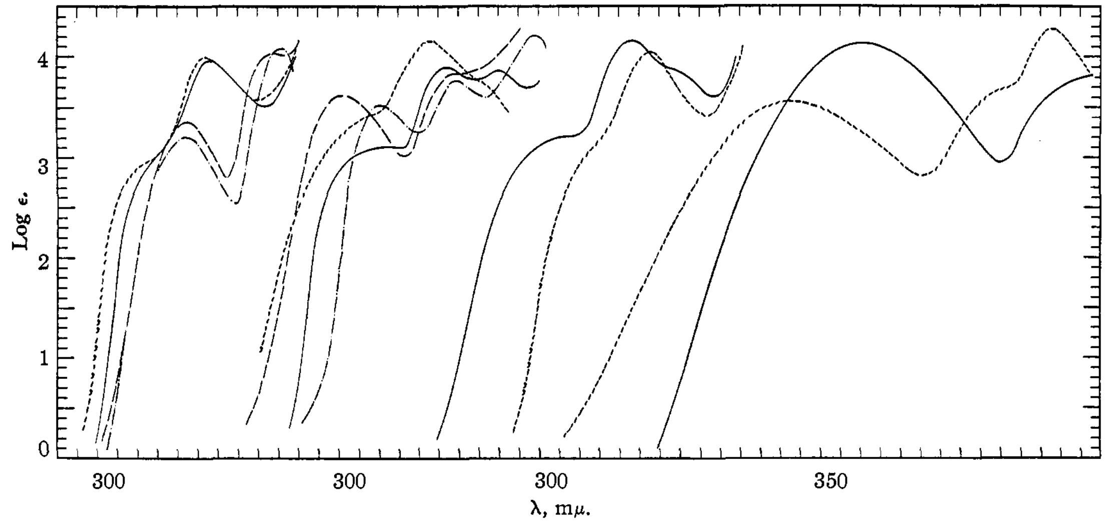
(7) Fehnel and Carmack, *ibid.*, **71**, 2932 (1949).

(8) *Cf.* Koch, quoted by Leonard and Sutton, *ibid.*, **70**, 1564 (1948). Further evidence in support of this conclusion has been obtained in a study of the spectra of substituted phenyl sulfones and will appear in a forthcoming paper in the present series.

(9) The nomenclature is that employed by Doub and Vandenbelt [THIS JOURNAL, **69**, 2714 (1947)] in describing the spectra of mono- and *p*-disubstituted benzene derivatives.

(10) Doub and Vandenbelt, reference in footnote 9.

(11) *Cf.* mesityl methyl ether (ref. 7), in which the primary band reaches a maximum at the same wave length as in mesitylene.



A single reference wave length is indicated for each group of curves; the wave length decreases toward the right and is marked at intervals of 10 mμ.

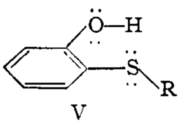
Fig. 2.—Absorption spectra of $C_6H_5SCH_3$, —; p-$CH_3C_6H_4SCH_3$, - - - - - -; $C_6H_5SC(CH_3)_3$, -·-·-; 2,4,6-$(CH_3)_3C_6H_2$-SCH_3, — — —; solvent, ethanol.

Fig. 3.—Absorption spectra of p-$HOC_6H_4SCH_3$ in EtOH, —, and in 0.01 N NaOEt, - - - - - -; o-$HOC_6H_4SCH_3$ in EtOH, —·—·—, and in 0.01 N NaOEt, — — —.

Fig. 4.—Absorption spectra of p-$NH_2C_6H_4SCH_3$ in EtOH, —, and in 2 N aq. HCl, - - - - -.

Fig. 5.—Absorption spectra of p-$NO_2C_6H_4SCH_3$, —; o-$NO_2C_6H_4SCH_3$, - - - - -; solvent, ethanol.

tion is somewhat surprising in view of the fact that steric effects would be expected to reduce appreciably the intensity of the absorption in this region.[4] It seems probable that the observed effect is to be attributed to hydrogen bonding in the ortho compound, the hydrogen bond being stabilized by resonance involving 5-covalent sulfur, as in structures V and VI.[12] The displacement of this band toward still longer wave lengths and higher intensities in the spectrum of the o-hydroxyphenyl methyl sulfide anion suggests significant contributions from the o-quinonoid form of the anion (IX).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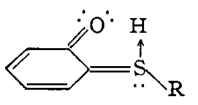
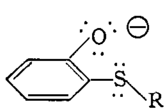
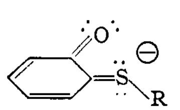

VI


VII


IX

In agreement with the results obtained by other investigators in studies of various other classes of substituted aromatic compounds,[5,10,13] we have found that the $-\ddot{\mathrm{O}}:^{\ominus}$ and $-\ddot{\mathrm{N}}\mathrm{H}_2$ substituents have very similar effects upon the absorption spectrum of the parent aromatic compound, while the $-NH_3^{\oplus}$ group causes little or no change in the spectrum of the parent compound. Thus the spectrum of p-aminophenyl methyl sulfide in neutral solution is almost identical with that of p-hydroxyphenyl methyl sulfide in alkaline solution, although in acid solution the spectrum of the amino compound becomes similar to that of unsubstituted phenyl methyl sulfide (Fig. 4).

In p-nitrophenyl methyl sulfide (Fig. 5) the methylmercapto group obviously behaves as an electron donor with respect to the benzene ring, as is indicated by the large displacement of the first primary absorption band ($\lambda_{\text{max.}}$ 338 mμ) toward longer wave lengths as compared with the corresponding band in the spectrum of either parent compound (phenyl methyl sulfide, $\lambda_{\text{max.}}$ 254 mμ[2]; nitrobenzene, $\lambda_{\text{max.}}$ 269 mμ[10]). Such behavior is characteristic of aromatic nitro compounds in which an electron-releasing substituent is located para to the strongly electrophilic nitro group.[10] It may be relevant to note, however, that the displacement is not so large as in the case of the p-nitrophenolate anion (λ_{max} 403 mμ),[10] although the first primary band in the spectrum of the phenolate anion ($\lambda_{\text{max.}}$ 235 mμ)[10] is at considerably *shorter* wave lengths than the corresponding band in the spectrum of phenyl methyl sulfide. This suggests that, unlike the $-\ddot{\mathrm{O}}:^{\ominus}$ substituent, which is capable of exerting only an electron-releasing ($+T$) effect, the $-\ddot{\underset{\cdot\cdot}{\mathrm{S}}}\mathrm{CH}_3$

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[12] Compare, for example, hydrogen bond formation in o-chlorophenol, o-methoxyphenol, catechol etc. (Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1942, pp. 320–326). The effect of intramolecular hydrogen bonding on the ultraviolet absorption spectra of aromatic hydroxy aldehydes and ketones has been discussed by Morton and Stubbs, *J. Chem. Soc.*, 1347 (1940).

[13] Kumler and Strait, THIS JOURNAL, **65**, 2349 (1943).

substituent may be capable of exerting either electron-releasing ($+T$) *or* electron-withdrawing ($-T$) effects, the latter effect being diminished or eliminated when the strongly electron-attracting —NO_2 group is present in the para position.[14]

TABLE I

ULTRAVIOLET ABSORPTION SPECTRA OF SUBSTITUTED PHENYL SULFIDES

Compound	Source[a]	Solvent[b]	Maxima[c] λ (mμ)	Log ε
p-Tolyl methyl sulfide	1	EtOH	(282)	3.01
			256	4.00
Mesityl methyl sulfide	2	EtOH	265	3.36
			223	4.03
p-Hydroxyphenyl methyl sulfide	3	EtOH	286	3.11
			256	3.89
			229	3.84
p-Hydroxyphenyl methyl sulfide	3	NaOEt	(292)	3.42
			263	4.14
p-Hydroxyphenyl *n*-amyl sulfide	3, 4	EtOH	(283)	3.10
			257	3.86
			229	3.94
p-Hydroxyphenyl *n*-amyl sulfide	3, 4	NaOEt	(292)	3.46
			265	4.20
o-Hydroxyphenyl methyl sulfide	5	EtOH	289	3.51
			252	3.76
			212	4.21
o-Hydroxyphenyl methyl sulfide	5	NaOEt	308	3.66
			(253)	3.82
p-Aminophenyl methyl sulfide	6	EtOH	(294)	3.22
			264	4.14
p-Aminophenyl methyl sulfide	6	HCl	(281)	3.13
			254	4.03
p-Nitrophenyl methyl sulfide	6	EtOH	338	4.12
			~215	3.81
o-Nitrophenyl methyl sulfide	7	EtOH	372	3.55
			(266)	3.71
			244	4.27

[a] Source references: (1) Eastman Kodak Co., redistilled; (2) see section on "Preparation of Compounds"; (3) Miller and Read, THIS JOURNAL, **55**, 1224 (1933); (4) sample obtained from Sharp and Dohme, Inc., through the courtesy of Dr. J. M. Sprague; (5) Holt and Reid, THIS JOURNAL, **46**, 2333 (1924); (6) Waldron and Reid, *ibid.*, **45**, 2399 (1923); (7) Foster and Reid, *ibid.*, **46**, 1936 (1924). [b] EtOH designates absolute ethanol; NaOEt designates 0.01 *N* sodium ethoxide prepared by dissolving sodium in absolute ethanol; HCl designates 2 *N* aqueous hydrochloric acid. [c] The wave lengths in parentheses refer to inflection points.

o-Nitrophenyl methyl sulfide (Fig. 5) shows the greatly decreased absorption at longer wave lengths which is characteristic of sterically hindered ortho compounds. In accordance with the prediction of theory for such compounds,[4] the first primary band in the spectrum of *o*-nitrophenyl methyl sulfide appears at shorter wave lengths than in the spectra of either of the monosubstituted parent compounds.

Experimental

The ultraviolet absorption measurements were made as described in a previous paper in this series.[2] The wave lengths and logarithms of the molar extinction coefficients at the absorption maxima and at prominent points of inflection are listed in Table I.

Preparation of Compounds.—Most of the compounds studied were prepared by procedures described in the literature, and were purified by two or more recrystallizations or redistillations immediately before determination of the spectra. Source references are given in Table I. **Mesityl methyl sulfide** was obtained by methylating 2,4,6-trimethylthiophenol[15] in the usual way with methyl iodide in methanolic sodium hydroxide solution. The crude product was obtained as an almost colorless oil, b. p. 110–115° at 14 mm.; yield 77%. Redistillation afforded a colorless middle fraction boiling at 112–113° at 14 mm.

Anal.[16] Calcd. for $C_{10}H_{14}S$: C, 72.22; H, 8.48. Found: C, 72.74; H, 8.46.

Summary

The ultraviolet absorption spectra of a number of *o*- and *p*-substituted phenyl alkyl sulfides have been determined. The preparation of mesityl methyl sulfide is described.

From a comparison of the absorption spectra of phenyl *t*-butyl sulfide and mesityl methyl sulfide with the spectra of other phenyl alkyl sulfides, it is concluded that steric factors influencing the resonance within the phenylmercapto group account satisfactorily for certain variations in the spectra of the phenyl sulfides. Some evidence for the ability of the sulfur atom in the alkylmercapto group to behave as an electron-acceptor with respect to an attached benzene ring is derived from a consideration of the spectra of hydroxy-, amino- and nitro-substituted derivatives of phenyl methyl sulfide.

SWARTHMORE, PA. RECEIVED DECEMBER 20, 1948

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[14] *Cf.* a similar suggestion made by Doub and Vandenbelt (ref. in footnote 9) with regard to the two-directional polarizability of the carboxyl group.

[15] Prepared in 71% yield by the reduction of mesitylenesulfonyl chloride with zinc dust and sulfuric acid; *cf.* Holtmeyer, *Z. Chem.*, 686 (1867).

[16] Semimicroanalysis performed by Mrs. Sarah M. Woods.