[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY]

Synthesis of Aryl Methyl Sulfoxides and Determination of the Conjugative Effect of the Methylsulfinyl Group[1]

BY F. G. BORDWELL AND PIERRE J. BOUTAN[2]

RECEIVED SEPTEMBER 13, 1956

Infrared analysis provides a reliable method for detecting the presence of sulfone impurities in samples of sulfoxides prepared by oxidation procedures. Using this guide it was observed that oxidation of aryl methyl sulfides with an equimolar quantity of hydrogen peroxide in acetic acid often gave sulfoxides contaminated with appreciable quantities of sulfones, which could not be removed by fractional crystallization. *p*-Methoxyphenyl methyl sulfide reacted under these conditions to give a pure sulfoxide at temperatures below 10°, but a considerable quantity of sulfone was formed at 25–30°. Formation of sulfone in the oxidation of aryl methyl sulfides was sometimes prevented by the presence of a strong electron-attracting group in the aromatic nucleus. Nitric acid oxidation of *m*-methanesulfonoxyphenyl, *m*-methoxyphenyl and *p*-nitrophenyl methyl sulfide was found to stop at the sulfoxide stage, whereas some sulfone is formed when one mole of hydrogen peroxide is used. The success of this method is ascribed to the reaction of the nitric acid with the sulfoxide formed to give an arylmethylhydroxysulfonium nitrate, $[ArS(OH)CH_3]^+ONO_2^-$, which resists further oxidation. Acidity constant measurements of *m*- and *p*-methylsulfinylbenzoic acids and phenols revealed an electron-pair accepting type of conjugative effect for the methylsulfinyl group (with consequent expansion of the valence shell of sulfur to ten or more electrons). Comparison of the ultraviolet absorption spectra of phenyl and *p*-hydroxyphenyl methyl sulfoxides failed to provide support for this conjugative effect. It is suggested that the ability of the methylsulfinyl group to act as an electron-pair donor in the photoexcited state of phenyl methyl sulfoxide may invalidate this method of assessing conjugation.

Synthesis of Aryl Methyl Sulfoxides

In order to continue our investigation of the conjugative ability of various sulfur groupings,[3] we wished to prepare *p*- and *m*-methylsulfinylphenols, *p*- and *m*-$(CH_3S^+{-}O^-)C_6H_4OH$. This did not appear to be more than a routine synthesis, since it has been reported on several occasions that sulfides are selectively oxidized to sulfoxides by the action of an equimolar quantity of hydrogen peroxide in acetic acid or acetone,[4] and both of the desired phenols were reported to have been obtained by this method.[5] Careful investigation revealed, however, that the compounds previously reported as sulfoxides by Zincke and Ebel[5] were in reality mixtures of sulfoxides and sulfones from which isolation of pure sulfoxide by fractional crystallization was extremely difficult. As a result, the study evolved initially into an evaluation of several preparative methods for aryl methyl sulfoxides.

Preparation of *p*- and *m*-hydroxyphenyl methyl sulfides was accomplished without difficulty by the route shown for the meta isomer. The ether cleavage occurred in better yield with hydrogen bromide in acetic acid containing about 10% of water than with hydrogen bromide in glacial acetic acid (92% *vs.* 69%), which is in line with previous experience.[6]

$$m\text{-}CH_3OC_6H_4MgBr \xrightarrow[(94\%)]{CH_3SSCH_3}$$

$$m\text{-}CH_3OC_6H_4SCH_3 \xrightarrow[(92\%)]{HBr\text{–}HOAc\text{–}H_2O} m\text{-}HOC_6H_5SCH_3$$

Oxidation of *p*-acetoxyphenyl methyl sulfide with one mole of hydrogen peroxide in acetic acid gave, after six recrystallizations, a product agreeing reasonably well in melting point with that reported by Zincke and Ebel[5a] as the sulfoxide. Hydrolysis gave material from which the only pure substance isolated was *p*-hydroxyphenyl methyl sulfone. The latter was identified by melting point and conversion to *p*-acetoxyphenyl methyl sulfone, which Zincke and Ebel inexplicably were unable to obtain by acetylation of *p*-hydroxyphenyl methyl sulfone. Oxidation of *p*-methoxyphenyl methyl sulfide under similar conditions also gave the corresponding sulfone as the most readily isolable product. Finally, the substance formed on oxidation of *p*-acetamidophenyl methyl sulfide was found to be a mixture containing the sulfone, rather than the pure sulfoxide, which Zincke and Jorg[7] believed they had obtained.

The relatively sharp melting point of these sulfoxide–sulfone mixtures is understandable since Rheinboldt and Giesbrecht[8] have shown that a sulfoxide and its corresponding sulfone often will form a continuous series of mixed crystals exhibiting sharp melting points. The formation of appreciable amounts of sulfones from oxidations of sulfides utilizing only one mole of hydrogen peroxide was surprising, however.

It seemed reasonable to us that oxidation beyond the sulfoxide stage might be dependent on the presence of groups such as *p*-CH_3O, *p*-AcO and *p*-AcNH, which are capable of electron release on demand. It would be anticipated that the sulfoxide group could conjugate more effectively with such electron-releasing groups than could a sulfide grouping.[9] This more effective conjugation conceivably could be sufficient to counteract the innately greater ability of the sulfide grouping to

---

[1] This investigation was supported in part by the American Petroleum Institute under Project 48B.

[2] Texas Co. Research Fellow, 1952–1954.

[3] (a) F. G. Bordwell and G. D. Cooper, THIS JOURNAL, **74**, 1058 (1952); (b) F. G. Bordwell and H. M. Anderson, *ibid.*, **75**, 6019 (1953); (c) M. T. Rogers, G. M. Barrow and F. G. Bordwell, *ibid.*, **78**, 1790 (1956); (d) F. G. Bordwell and Pierre J. Boutan, *ibid.*, **78**, 87 (1956); (e) **78**, 854 (1956).

[4] (a) See, for example, O. Hinsberg, *Ber.*, **41B**, 2836 (1908); (b) M. Gazdar and S. Smiles, *J. Chem. Soc.*, **93**, 1836 (1908).

[5] (a) Th. Zincke and C. Ebel, *Ber.*, **47B**, 1100 (1914); (b) **47B**, 923 (1914).

[6] A. Luttringhaus and G. Saaf, *Angew. Chem.*, **51**, 916 (1938).

[7] Th. Zincke and P. Jorg, *Ber.*, **42B**, 3362 (1909).

[8] H. Rheinboldt and E. Giesbrecht, THIS JOURNAL, **68**, 973 (1946).

[9] Divalent sulfur groupings are reluctant to enter into this type of conjugation (see ref. 3e) whereas the methylsulfinyl group can do so effectively (see below). Our results do not agree with the conclusion of E. Rothstein and co-workers [*J. Chem. Soc.*, 3991 (1953)] that the sulfoxide and sulfonium groups[3e] are not capable of valence shell expansion.

provide electrons to the oxidizing agent and to make the sulfoxide to sulfone stage of the oxidation competitive with the sulfide to sulfoxide stage. With this in mind we carried out oxidations in which strong electron-withdrawing groups were substituted for the AcO– or AcNH– groups. This approach was partially successful, since the oxidations stopped at the sulfoxide stage with *m*- and *p*-3,5-$(NO_2)_2C_6H_3COO$– and *p*-Cl_3CCONH– groups present in the ring of phenyl methyl sulfide. However, oxidation of *m*-$CH_3SO_2OC_6H_4SCH_3$ gave some sulfone.

Careful hydrolysis of *p*-$[3,5\text{-}(NO_2)_2C_6H_3COO]\text{-}C_6H_4(S^+\text{–}O^-)CH_3$ gave the desired *p*-hydroxyphenyl methyl sulfoxide, m.p. 103.5–104°. Zincke and Ebel[5] reported a melting point of 91–92°, which corresponds roughly to a mixture of about equal parts of sulfoxide and sulfone. Attempts to isolate pure *m*-hydroxyphenyl methyl sulfoxide by hydrolysis of *m*-$[3,5\text{-}(NO_2)_2C_6H_3COO]C_6H_4(S^+\text{–}O^-)CH_3$ were unsuccessful, however.

Since the peaks in the infrared for sulfone (7.41–7.69 μ and 8.62–8.93 μ regions) and for sulfoxide (9.43–9.71 μ)[10] are separated, infrared analysis provides a sensitive and convenient method for detecting the presence of sulfone in sulfoxide samples. The presence of considerable quantities of sulfone in the products from oxidation of *p*-methoxyphenyl, *p*-acetoxyphenyl and *p*-acetamidophenyl methyl sulfides by one mole of hydrogen peroxide in acetic acid was verified by infrared analysis. In contrast, the samples of *m*- and *p*-3,5-dinitrobenzoxyphenyl, *p*-trichloroacetamidophenyl and *p*-hydroxyphenyl methyl sulfoxides described above were shown by infrared analysis to be free of sulfone contamination. The products from oxidations of *m*-$CH_3SO_2OC_6H_4SCH_3$ and *p*-$NO_2C_6H_4SCH_3$ were found, however, to be contaminated with appreciable quantities of sulfone.

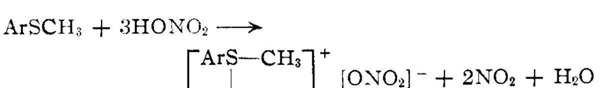
Formation of sulfone from *m*-$CH_3SO_2OC_6H_4SCH_3$ and *p*-$NO_2C_6H_4SCH_3$ and one mole of hydrogen peroxide necessitates abandoning our theory that the presence of electron-donor groups in *ortho* or *para* positions is the only factor responsible for making the sulfoxide to sulfone oxidation competitive with the sulfide to sulfoxide oxidation. Apparently this is a property of many aryl methyl sulfides which has not been recognized previously. Oxidation of aliphatic sulfides with one mole of oxidizing agents does not appear to lead to sulfone formation.[11] Some aryl sulfides and thiophene derivatives may give sulfones, however. For example, benzothiophene when oxidized with one mole of hydrogen peroxide gave only sulfone, since no peak for sulfoxide appeared in the infrared spectrum of the product.[12]

Temperature was observed to exert a strong influence on the quantity of sulfone formed in some instances. *p*-Methoxyphenyl methyl sulfide was found to be oxidized selectively to the sulfoxide at temperatures below 10° with hydrogen peroxide in acetic acid–acetic anhydride, but at 25–30° considerable quantities of sulfone were formed. On the other hand, *m*-methoxyphenyl methyl sulfide and benzothiophene gave large amounts of sulfone even at temperatures below 0°.

A successful synthesis of *m*-hydroxyphenyl methyl sulfoxide was finally accomplished by a nitric acid oxidation of *m*-methanesulfonoxyphenyl methyl sulfide,[13] followed by alkaline hydrolysis. Judging from their method of preparation and from the fact that the oil Zincke and Ebel[5b] took to be the sulfoxide gave a benzoate melting at 83–84°, it seems likely that they were working with a mixture of the sulfoxide and sulfone. Our sample of *m*-hydroxyphenyl methyl sulfoxide was obtained in crystalline form, m.p. 61–62°. The benzoate of this sample, which was shown by infrared analysis to be free of sulfone, melted at 91–92°. The benzoate of *m*-hydroxyphenyl methyl sulfone melted at 94–95°, and a mixture of about equal parts of the sulfoxide and sulfone melted at 81–86°, the major part of the sample melting near the m.p. reported by Zincke and Ebel.[5b] *m*-Methoxyphenyl methyl sulfoxide was obtained by methylating *m*-hydroxyphenyl methyl sulfoxide with diazomethane.

Oxidation with the aid of nitric acid[14] was found in the present investigation to be capable of producing sulfoxides free of sulfones from the three aryl methyl sulfides for which other methods failed. The successful oxidation of *m*-methanesulfonoxy and *m*-methoxyphenyl methyl sulfides free of sulfone was achieved by oxidation of the sulfide with acetic anhydride–nitric acid, according to the directions used by Pollard and Robinson for the preparation of *o*-methoxyphenyl methyl sulfoxide.[15] Oxidation of *p*-nitrophenyl methyl sulfide with excess concentrated nitric acid gave pure *p*-nitrophenyl methyl sulfoxide, whereas the product from oxidation with one mole of hydrogen peroxide was contaminated with the sulfone.

The failure of nitric acid oxidations of sulfides to proceed beyond the sulfoxide stage, even in the presence of a large excess of oxidizing agent, is probably due to the formation of a sulfonium salt. Sulfoxides are weak bases and no doubt exist principally as sulfonium salts in the presence of strong acids, such as nitric acid. The sulfonium salt would be expected to be resistant to oxidation.



$$ArSCH_3 + 3HONO_2 \longrightarrow \left[\begin{array}{c} ArS\text{—}CH_3 \\ | \\ OH \end{array}\right]^+ [ONO_2]^- + 2NO_2 + H_2O$$

To test the effect of strong acids in controlling the stage of oxidation, the reaction of *p*-nitrophenyl methyl sulfide with one mole of hydrogen peroxide in acetic acid containing two moles of trifluoroacetic acid was investigated. After standing for 72 hr. at 25–30°, an infrared analysis showed

---

(10) See the table compiled by F. Miller in "Organic Chemistry, An Advanced Treatise," edited by H. Gilman, John Wiley and Sons, Inc., New York, N. Y., p. 149.

(11) A study of the oxidation of aryl methyl sulfides and other types of sulfides is being continued in this Laboratory.

(12) B. B. Lampert, Doctoral Dissertation, Northwestern University, 1951, isolated only sulfone from the oxidation of benzothiophene with an equimolar quantity of perbenzoic acid.

(13) As pointed out recently by J. H. Looker and D. N. Thatcher, *J. Org. Chem.*, **19**, 784 (1954), the methanesulfonoxy group is an excellent blocking group for phenols since methanesulfonates of phenols are readily prepared, nicely crystalline, stable in aqueous acid and easily hydrolyzed in dilute base.

(14) C. Marker, *Ann.*, **136**, 89 (1865).

(15) A. Pollard and R. Robinson, *J. Chem. Soc.*, 3090 (1926).

the presence of a strong sulfoxide band at 9.5 μ and no sulfone bands. A sample treated in an identical manner except for omission of trifluoroacetic acid showed a strong sulfoxide band but also showed two weaker sulfone bands at 7.6 and 8.6 μ. Oxidation of benzothiophene with hydrogen peroxide in trifluoroacetic acid gave a product which showed a strong sulfoxide band and no sulfone bands, but pure sulfoxide has not as yet been isolated.

Conjugative Effects of the Methylsulfinyl Group

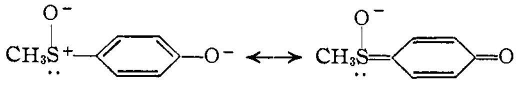
The acidity constants of *m*- and *p*-methylsulfinylbenzoic acids and phenols are summarized in Table I. From Hammett σ-constants for the methylsulfinyl group it is apparent that this group, when substituted in a *p*-position, is more effective in increasing the acidity of phenol than of benzoic acid. However, when substituted in a *m*-position the acidifying effects are of a comparable magnitude (the σ-constants differ by only 0.02 unit). These results suggest conjugation of the type indicated for the *p*-methylsulfinylphenolate ion.

TABLE I

ACIDITY CONSTANTS OF *m*- AND *p*-METHYLSULFINYLBENZOIC ACIDS AND PHENOLS AT 25°

Substituent	Benzoic acids[a]			Phenols[b]		
	pK_a	σ	$\sigma_p - \sigma_m$	pK_a	σ	$\sigma_p - \sigma_m$
m-CH_3SO	4.97	+0.51[c]		8.75	+0.53	
p-CH_3SO	5.01	+0.48[c]	−0.03	8.28	+0.73	+0.20

[a] Measured by Dr. Glenn D. Cooper in 50% alcohol. [b] Determined in water. [c] C. C. Price and J. J. Hydock, THIS JOURNAL, **74**, 1943 (1952), report σ-values of +0.49 and +0.45 for the *m*- and *p*-methylsulfinyl groups.



The methylsulfinyl group resembles the methylsulfonyl[3a–c] and dimethylsulfonio[3d] groups in its ability to enter into electron-pair acceptor type resonance interactions with consequent expansion of the valence shell of sulfur to ten or more electrons. The differences between the σ-constants of *para* groups for benzoic acids and phenols, which may be taken as an indication of the extent of conjugation are: CH_3SO_2, 0.26(σ-unit)[3a]; $(CH_3)_2S^+$, 0.26[3d]; $CH_3S^+{-}O^-$, 0.25. Comparable differences for other electron-attracting groups are *p*-NO_2, +0.49; *p*-$COCH_3$, +0.44[3a]; *p*-$(CH_3)_3N^+$, −0.19 (no resonance).[3d] In contrast, divalent sulfur groupings show a reluctance to enter into conjugation of this type.[3e]

The electron-pair acceptor type conjugation for CH_3SO_2 and $(CH_3)_2S^+$ groups manifests itself in the ultraviolet spectra of the *p*-substituted phenols, as well as in the acidity constants.[3d] This is not true for the methylsulfinyl group.

Phenyl methyl sulfoxide has an intense primary band at 235 mμ[16] which corresponds to the band at 217 mμ for phenyl methyl sulfone.[17] The methylsulfinyl group therefore exhibits a considerably stronger electronic effect in the photoexcited state than does the methylsulfonyl group ($\Delta\lambda CH_3\ddot{S}O$ = 31.5 *vs.* $\Delta\lambda CH_3SO_2$ = 13.5).[18] The methylsulfinyl group appears in this respect to resemble the methylthio group ($\Delta\lambda CH_3S$ 50.5) more than the methylsulfonyl group. This suggests that the methylsulfinyl group may be entering into electron-donor type conjugation in the photoexcited state, since the high Δλ value of the methylthio group is probably due to electron-donor resonance.[3e] The Δλ value for the primary band in *p*-methylsulfinylphenol is 38.5 mμ (Table II), which is exactly the sum of the Δλ values for the phenolic hydroxyl group (Δλ 7)[18] and the methylsulfinyl group (Δλ 31.5). Conjugation of groups usually results in a Δλ value considerably greater than the additive value,[18] so this result suggests no conjugation. However, it seems possible that the methylsulfinyl group may exhibit a different type of electronic behavior in the photoexcited state when *para* to a hydroxyl group, which may inhibit its electron-pair donor properties and elicit its electron-acceptor properties, than it does in phenyl methyl sulfoxide itself.

On this basis it might be anticipated that *p*-$COCH_3$, *p*-COOH and *p*-NO_2 groups might evoke electron-donor resonance from the methylsulfinyl group leading to Δλ values greater than the sum of the individual values. This does not appear to be the case, however (Table II), the spectra being similar to those of *p*-disubstituted benzenes with two electron-acceptor groups.[18]

TABLE II

PRINCIPAL MAXIMA IN THE ULTRAVIOLET SPECTRA OF SOME ARYL METHYL SULFOXIDES

Methyl sulfoxide	Primary max., mμ[a]	log ε	Secondary max., mμ	log ε
Phenyl	235	3.60		
p-Hydroxyphenyl	242	4.05		
p-Hydroxyphenyl[c]	268	4.26		
m-Hydroxyphenyl	240[b]	3.50	282	3.40
m-Hydroxyphenyl[c]	245[b]	3.90	307	3.50
p-Acetophenyl	235	4.00	260	3.97
p-Nitrophenyl	246	3.85	285	3.84
p-Carboxypheny	247	3.91		
p-Carboxyphenyl[c]	252	3.86		
m-Carboxyphenyl			280[b]	2.70
m-Carboxyphenyl[c]			280[b]	2.70

[a] Δλ values are obtained from these by subtracting 203.5 mμ [b] Shoulder. [c] 0.01 *N* NaOH.

Experimental[19]

***m*-Methoxyphenyl Methyl Sulfide.**—*m*-Bromoanisole (94.0 g., 0.5 mole) was converted to the Grignard reagent with 14.4 g. (0.6 g. atom) of magnesium in 500 cc. of dry ether. The addition took 3 hr. and the solution was refluxed 30 min. longer. Methyl disulfide (32 g., 0.34 mole) in 300 cc. of anhydrous ether was added dropwise and the solution refluxed for an additional 45 min. A solution of 200 cc. of water and 60 cc. of concd. hydrochloric acid was added dropwise with external cooling to liberate methyl mercaptan (trap) and dissolve the magnesium salts. The ether was separated and the aqueous solution washed with 400 cc. of ether in 4 portions. The combined ether extracts were dried over sodium hydroxide pellets, the ether distilled and the product fractionated through a 22-cm. vacuum-jacketed Vigreux column to yield 49.0 g. (65% based on *m*-

---

[16] H. P. Koch, *J. Chem. Soc.*, 2892 (1950).

[17] E. A. Fehnel and M. Carmack, THIS JOURNAL, **71**, 231 (1949).

[18] See the excellent discussion of such effects using this terminology by L. Doub and J. M. Vandenbelt, *ibid.*, **69**, 2714 (1947).

[19] Microanalyses were carried out by Mrs. Malcolm White, Miss Joyce Sorenson and Miss H. Beck. Melting points are uncorrected.

bromoanisole, 94% based on methyl disulfide) of product, b.p. 125–127° at 16–17 mm. The yield was not increased by use of a nitrogen atmosphere or an increased quantity of methyl disulfide; the yield of Grignard reagent appears to be the limiting factor.

Anal. Calcd. for $C_8H_{10}SO$: C, 62.31; H, 6.53. Found: C, 62.42; H, 6.59.

p-Methoxyphenyl methyl sulfide, m.p. 25–26°, was prepared in 94% yield from *p*-bromoanisole by the method described for its *m*-isomer.

***m*-Hydroxyphenyl Methyl Sulfide.**—A solution of 58.0 g. (0.38 mole) of *m*-methoxyphenyl methyl sulfide, 65 g. (0.80 mole) of hydrogen bromide, 30 cc. of 48% hydrobromic acid and 400 cc. of glacial acetic acid was refluxed for 6 hr. The solvent was removed under reduced pressure and the residual cherry-red oil was poured into 300 cc. of ice-water. The mixture was extracted with 400 cc. of ether in 4 portions, the ether extracts were combined, washed with water and extracted with 200 cc. of 15% potassium hydroxide solution. The basic solution was acidified with concentrated hydrochloric acid and extracted with 400 cc. of ether. Distillation of the ether and fractionation of the residual oil through a 22 cm. Vigreux column gave 49 g. (92.5%) of a colorless liquid, b.p. 154-156° at 17–18 mm., n^{30}_{D} 1.6132, m.p. 29–29.5°. Zincke and Ebel[5b] reported b.p. 148-151° at 15 mm., m.p. 15°.

Anal. Calcd. for C_7H_8OS: C, 59.96; H, 5.75. Found: C, 59.71; H, 5.81.

***m*-Acetoxyphenyl Methyl Sulfide.**—Ice (50 g.) followed by 5.0 ml. (0.05 mole) of acetic anhydride was added to a solution of 5.0 g. (0.036 mole) of *m*-hydroxyphenyl methyl sulfide in 20 cc. of 15% aqueous potassium hydroxide. The solid which separated out after a few minutes of shaking was collected, washed with water and recrystallized from benzene-hexane to give 5.5 g. (83%) of white needles, m.p. 40-41°, b.p. 146–147° at 17–18 mm.

Anal. Calcd. for $C_9H_{10}O_2S$: C, 59.33; H, 5.53. Found: C, 59.44; H, 5.38.

***m*-Methylthiophenyl 3,5-Dinitrobenzoate.**—A solution of 10.5 g. (0.075 mole) of *m*-hydroxyphenyl methyl sulfide and 18.5 g. (0.080 mole) of freshly prepared 3,5-dinitrobenzoyl chloride in 100 cc. of dry pyridine was refluxed for 1.5 hr., cooled and poured into 500 cc. of 5% sulfuric acid. The precipitate was collected on a filter, washed with 5% sodium hydroxide solution, then with 5% hydrochloric acid and finally with water. After recrystallization from benzene, 22.2 g. (89.5%) of material, m.p. 140–141°, was obtained.

Anal. Calcd. for $C_{14}H_{10}O_8N_2S$: C, 50.03; H, 3.02. Found: C, 49.44; H, 3.22.

***m*-Methylthiophenyl Methanesulfonate.**—Methanesulfonyl chloride (22.8 g., 0.20 mole) was added dropwise at a temperature not exceeding 5° to a solution of 14 g. (0.10 mole) of *m*-hydroxyphenyl methyl sulfide and 200 cc. of dry pyridine. The solution turned yellow and a crystalline material began to appear. Stirring was discontinued, and the reaction mixture was allowed to stand at 0–5° for 24 hr. The mixture was poured into a mixture of 250 cc. of concentrated hydrochloric acid and 300 g. of ice. The precipitate obtained was filtered and recrystallized from aqueous methanol, then from chloroform-pentane to give 18.7 g. (86%) of white material, m.p. 38–39°.

Anal. Calcd. for $C_8H_{10}O_3S_2$: C, 44.01; H, 4.62. Found: C, 44.05; H, 4.44.

***p*-Hydroxyphenyl Methyl Sulfide.**—Cleavage of *p*-methoxyphenyl methyl sulfide according to the directions of Suter and Hansen[20] gave 69% of a material, m.p. 83–84°. The yield no doubt could be improved by adding aqueous hydrogen bromide as described for the *m*-isomer.

***p*-Methylthiophenyl Acetate.**—Acylation of *p*-hydroxyphenyl methyl sulfide with acetic anhydride by the Schotten–Baumann procedure gave 80% yield of product, m.p. 43.5–44°. Zincke and Ebel reported[5a] a m.p. of 44°.

***p*-Methylthiophenyl 3,5-Dinitrobenzoate.**—Esterification of *p*-hydroxyphenyl methyl sulfide with 3,5-dinitrobenzoyl chloride in pyridine at 0° by the method used for the *m*-isomer gave 88% of material, m.p. 171–172°.

Anal. Calcd. for $C_{14}H_{10}O_8N_2S$: C, 50.03; H, 3.02. Found: C, 50.44; H, 3.14.

Preparation of Sulfones.—The sulfones were generally prepared by the oxidation of the sulfide in refluxing acetic acid with a fourfold excess of hydrogen peroxide. After a reflux period of 15–30 minutes, water equal to the amount of acetic acid used was added and the solution cooled. Filtration or extraction with chloroform gave the desired product in yields varying from 80–90%. Purified samples of these sulfones were used in spectral work for the identification of materials obtained in the subsequent preparations of sulfoxides. The preparation of *m*-methoxyphenyl methyl sulfone is a typical example.

***m*-Methoxyphenyl Methyl Sulfone.**—Hydrogen peroxide (30 ml. of 30%, 0.27 mole) was added to a solution of 7.7 g. (0.05 mole) of *m*-methoxyphenyl methyl sulfide in 40 cc. of glacial acetic acid. The solution started to reflux immediately and it was kept at reflux for 30 min. Addition of water followed by cooling precipitated an oil which could not be crystallized. It was extracted with 100 ml. of chloroform, and the chloroform extracts were combined, washed with saturated sodium bicarbonate solution, then water and dried over sodium sulfate. Evaporation of the solvent followed by distillation of the residual material gave 8.0 g. (86%) of a colorless sirup, b.p. 140–150° at 0.2–0.3 mm.

Anal. Calcd. for $C_8H_{10}O_3S$: C, 51.60; H, 5.41. Found: C, 51.13; H, 5.62.

***p*-Methoxyphenyl Methyl Sulfone.**—Oxidation of *p*-methoxyphenyl methyl sulfide with hydrogen peroxide in acetic acid gave 92.5% yield of a product, m.p. 121.5–122°. Suter and Hansen reported[20] a m.p. of 119–120°.

Anal. Calcd. for $C_8H_{10}O_3S$: C, 51.60; H, 5.41. Found: C, 51.80; H, 5.38.

***m*-Hydroxyphenyl Methyl Sulfone.**—Cleavage of *m*-methoxyphenyl methyl sulfone with 48% hydrobromic acid according to the directions of Bordwell and Cooper[3a] for the preparation of *p*-hydroxyphenyl methyl sulfone gave 60% yield of a material m.p. 83–84°. A melting point of 84–85° has been reported.[3a]

***m*-Methylsulfonylphenyl Acetate.**—Oxidation of *m*-methylthiophenyl acetate with 30% hydrogen peroxide in refluxing acetic acid gave 84% yield of a material, m.p. 68–69°, which was identical with the product obtained from *m*-methylsulfonylphenol and acetic anhydride by the Schotten–Baumann procedure.

Anal. Calcd. for $C_9H_{10}O_4S$: C, 50.46; H, 4.70. Found: C, 50.28; H, 4.71.

***m*-Methylsulfonylphenyl 3,5-Dinitrobenzoate.**—Esterification of *m*-methylsulfonylphenol in pyridine with 3,5-dinitrobenzoyl chloride gave 62.5% yield of a material, m.p. 164.5–165.5°, after recrystallization from methanol. Oxidation of *m*-methylthiophenyl 3,5-dinitrobenzoate with excess hydrogen peroxide in acetic acid gave a similar product, as judged by mixed melting point determinations.

Anal. Calcd. for $C_{14}H_{10}O_8N_2S$: C, 45.90; H, 2.75. Found: C, 45.66; H, 2.83.

***m*-Methylsulfonylphenyl Benzoate.**—Fifty grams of ice followed by 0.70 g. (0.005 mole) of benzoyl chloride were added to a solution of 0.5 g. (0.0029 mole) of *m*-methylsulfonylphenol in 5 cc. of 10% sodium hydroxide solution. The reaction mixture was shaken for 10 minutes, then extracted with chloroform. Evaporation of the solvent and crystallization of the residue from benzene–hexane gave 0.52 g. (64%) of material, m.p. 94–95°.

Anal. Calcd. for $C_{14}H_{12}O_4S$: C, 60.85; H, 4.38. Found: C, 60.83; H, 4.08.

***m*-Methylsulfonylphenyl Methanesulfonate.**—Hydrogen peroxide (4.4 ml. of 50%, 0.04 mole) was added to a solution of 10 ml. of glacial acetic acid and 1.09 g. (0.005 mole) of *m*-methylthiophenyl methanesulfonate. The solution was refluxed 15 minutes, and then 20 cc. of hot water was added. The product which separated out on cooling was filtered and recrystallized from 50% aqueous ethanol to give 1.1 g. (88%) of white leaves, m.p. 136.5–137.5°.

Anal. Calcd. for $C_8H_{10}O_5S_2$: C, 38.39; H, 4.03. Found: C, 38.92; H, 4.06.

***p*-Hydroxyphenyl Methyl Sulfone.**—Cleavage of *p*-methoxyphenyl methyl sulfone according to the method of Bordwell and Cooper[3a] gave 60% yield of a material m.p. 95–96°. These authors report a m.p. 95.5–96.5°. The hydrolysis of *p*-methylsulfonylphenyl acetate obtained by the oxidation of *p*-methylthiophenyl acetate with 30% hydrogen

---

(20) C. M. Suter and H. L. Hansen, THIS JOURNAL, **54**, 4100 (1932).

peroxide gave a product which melted at 95–96° and did not depress the m.p. of *p*-methylsulfonylphenol.

***p*-Methylsulfonylphenyl Acetate.**—Oxidation of *p*-methylthiophenyl acetate with excess 30% hydrogen peroxide gave 88% yield of a product, m.p. 101–102°, which did not depress the m.p. of the material obtained by acylation of *p*-methylsulfonylphenol. Zincke and Ebel[5a] reported that they were unable to prepare this compound by acylation.

Anal. Calcd for $C_9H_{10}O_4S$: C, 50.46; H, 4.70. Found: C, 50.66; H, 4.70.

***p*-Methylsulfonylphenyl 3,5-Dinitrobenzoate.**—The oxidation of a sample of *p*-methylthiophenyl 3,5-dinitrobenzoate gave an 88% yield of a material, m.p. 181–182°, which was identical with a sample prepared by esterifying *p*-methylsulfonylphenol.

Anal. Calcd. for $C_{14}H_{10}O_8N_2S$: C, 45.90; H, 2.75. Found: C, 46.13; H, 2.83.

Oxidation of Sulfides for the Preparation of Sulfoxides. *p*-Hydroxyphenyl Methyl Sulfide.—The oxidation of *p*-hydroxyphenyl methyl sulfide with an equivalent amount of hydrogen peroxide in acetic acid, acetic anhydride or acetone, at temperatures ranging from 0 to 25° led to the formation of a brown oil which could not be purified by crystallization and which pyrolyzed on distillation. Oxidation with sodium hypochlorite in methanol gave similar results.

***p*-Acetoxyphenyl Methyl Sulfide.**—Hydrogen peroxide (11 ml. of 30%, 0.10 mole) was added slowly to 15 g. (0.082 mole) of *p*-acetoxyphenyl methyl sulfide in 60 cc. of glacial acetic acid. The solution was kept in an ice-bath during the addition, at room temperature for 8 days, then poured into ice-water. The material which separated was filtered and recrystallized twice from benzene–hexane to give 6.9 g. of white leaflets, m.p. 96–99°. Three additional recrystallizations brought the m.p. to 98–99°. This material did not appreciably depress the m.p. of an authentic sample of *p*-acetoxyphenyl methyl sulfone and showed on infrared analysis the presence of sulfoxide and sulfone bands.

Four grams of this material was hydrolyzed with 100 cc. of an aqueous 10% sodium hydroxide solution. The product obtained, m.p. 94.5–95°, did not depress the melting point of *p*-methylsulfonylphenol and had an infrared absorption spectrum identical with that of this compound.

Similar results were obtained when lower temperatures (0 to 5°) or solvents such as acetic anhydride or acetone were used. Materials melting between 93 and 99° were always obtained, and laborious recrystallizations gave impure sulfone, m.p. 98–99°. Zincke and Ebel[5a] have reported a melting point of 97–98° for *p*-acetoxyphenyl methyl sulfoxide.

***p*-(3,5-Dinitrobenzoxy)-phenyl Methyl Sulfide.**—*p*-(3,5-Dinitrobenzoxy)-phenyl methyl sulfide was oxidized with hydrogen peroxide according to the procedure described below for its *m*-isomer. After a recrystallization from aqueous methanol, an 80% yield of ***p*-(3,5-dinitrobenzoxy)-phenyl methyl sulfoxide**, m.p. 156–157°, was obtained.

Anal. Calcd. for $C_{14}H_{10}O_7N_2S$: C, 48.00; H, 2.88. Found: C, 47.88; H, 2.94.

Nine grams (0.026 mole) of *p*-(3,5-dinitrobenzoxy)-phenyl methyl sulfoxide was added to 100 cc. of 10% aqueous sodium hydroxide solution and stirred for 48 hr. at 30°. The solution was saturated with carbon dioxide and extracted with ether using a continuous liquid–liquid extractor. The ether extract was dried over magnesium sulfate and filtered. Evaporation of the filtrate followed by crystallization of the residue from 5% chloroform in toluene gave 2.35 g. (58%) of colorless plates of ***p*-hydroxyphenyl methyl sulfoxide**, m.p. 103.5–104°. An infrared analysis showed this material to be free of sulfone.

Anal. Calcd. for $C_7H_8O_2S$: C, 53.82; H, 5.16. Found: C, 53.81; H, 5.16.

***m*-Methoxyphenyl Methyl Sulfide.**—The oxidation of *m*-methoxyphenyl methyl sulfide was carried out with hydrogen peroxide and with nitric acid:

Hydrogen Peroxide Oxidation.—A solution of hydrogen peroxide (0.57 ml. of 30%, 0.005 mole) in 5 cc. of acetic anhydride was added slowly to 0.77 g. (0.005 mole) of *m*-methoxyphenyl methyl sulfide in 5 cc. of acetic acid and 5 cc. of acetic anhydride. The solution was kept at −20° during the addition, then at 10–15° for an additional 24 hr. The solvents were removed under reduced pressure and the residual oil was taken up in chloroform. An infrared spectrum of the carefully washed and dried chloroform solution revealed the presence of sulfoxide and sulfone bands (richer in sulfone). The same oxidation was repeated at 0° and at 30° but with similar results.

Nitric Acid Oxidation.—*m*-Methoxyphenyl methyl sulfide (5 g., 0.0325 mole) was oxidized with nitric acid (d. 1.5) in acetic anhydride according to the procedure of Pollard and Robinson.[15] After 15 hr. at 0°, the solution was neutralized and extracted with chloroform. Evaporation of the solvent followed by distillation of the residual oil gave 3.0 g. (54%) of a sirupy material, b.p. 122–123° at 0.7 mm. Redistillation gave a colorless, very hygroscopic sample of ***m*-methoxyphenyl methyl sulfoxide**, b.p. 111–112° at 0.2–0.3 mm. An infrared spectrum showed a sulfoxide band and no sulfone peaks.

Anal. Calcd. for $C_8H_{10}O_2S$: C, 56.46; H, 5.92. Found: C, 56.16; H, 6.13.

m-Methoxyphenyl methyl sulfoxide was also prepared by methylation of *m*-hydroxyphenyl methyl sulfoxide. An ethereal solution of diazomethane (0.20 mole) prepared according to the directions of Arndt[21] from nitrosomethylurea was added to 2.4 g. (0.0154 mole) of *m*-hydroxyphenyl methyl sulfoxide (see below) in 100 cc. of ether. The solution turned from deep yellow to light yellow while nitrogen was evolved. After 12 hr., the ether and excess diazomethane were distilled. The yellow residual oil which could not be crystallized was distilled to give 2.1 g. (80%) of a sirupy material, b.p. 111–112° at 0.2–0.3 mm., n^{26}_D 1.5720. An infrared spectrum of this material was identical with that of the sample prepared by nitric acid oxidation.

***m*-Hydroxyphenyl and *m*-Acetoxyphenyl Methyl Sulfides.**—Oxidation of *m*-hydroxyphenyl methyl sulfide with an equimolar quantity of hydrogen peroxide in acetic acid for 24 hr. at 10–20° gave a yellow oil which could not be crystallized and which pyrolyzed on distillation.

A similar result was obtained in an attempted oxidation of *m*-acetoxyphenyl methyl sulfide in acetic acid–acetone solution. When acetic anhydride was used as the solvent, a 40% yield of *m*-methylsulfonylphenyl acetate, m.p. 67–69°, was obtained. When the latter experiment was carried out at temperatures below 10° material of lower m.p. was obtained which gave an infrared spectrum exhibiting both sulfoxide and sulfone bands.

***m*-(3,5-Dinitrobenzoxy)-phenyl Methyl Sulfide.**—Hydrogen peroxide (1.25 ml. of 30%, 0.011 mole) was added dropwise to a suspension of 3.3 g. (0.010 mole) of *m*-methylthiophenyl 3,5-dinitrobenzoate in 50 cc. of acetone and 50 cc. of acetic acid maintained at 5°. The solution was allowed to stand at 25° until the solid had dissolved (4–5 days). The solvent was distilled under vacuum, the temperature being kept below 25°. The solid residue obtained was washed with water and recrystallized from dilute methanol, then benzene, to give 3.1 g. (88.5%) of ***m*-(3,5-dinitrobenzoxy)-phenyl methyl sulfoxide**, small cream-colored plates, m.p. 135–135.5°.

Anal. Calcd. for $C_{14}H_{10}O_7N_2S$: C, 48.00; H, 2.88. Found: C, 47.99; H, 2.85.

This material was hydrolyzed with 100 cc. of 10% sodium hydroxide at room temperature for 48 hr. The basic solution was saturated with carbon dioxide and extracted with ether. The ether extract was dried and the ether distilled; an infrared spectrum of the crude product was identical with that of a crystalline sample of *m*-hydroxyphenyl methyl sulfoxide prepared *via* the oxidation of the methanesulfonate derivative. This present sample could not be crystallized, however, and pyrolyzed on distillation.

***m*-Methanesulfonoxyphenyl Methyl Sulfide.**—The oxidizing agents used were hydrogen peroxide and nitric acid:

Hydrogen Peroxide Oxidations.—Ten ml. of acetic acid and 1.11 ml. (0.010 mole) of 30% hydrogen peroxide were added dropwise to a solution of 2.0 g. (0.0092 mole) of *m*-methanesulfonoxyphenyl methyl sulfide and 10 cc. of acetic anhydride at −10°. The solution was allowed to stand 48 hr. at 10°, then poured in ice-water and neutralized with sodium carbonate. The white crystalline material which separated was filtered and crystallized from aqueous methanol to give 2.0 g. (96%) of material, m.p. 85–90°. An infrared analysis showed these crystals to be a mixture of sulfoxide and sulfone (richer in the former). One gram of this material was hydrolyzed completely in 40 minutes at steam-bath temperature by 15 cc. of a 7.5% sodium hydroxide

---

[21] F. Arndt, *Org. Syntheses*, **15**, 3 (1935).

solution: infrared analysis of the oil obtained by extraction with chloroform showed the presence of a sulfoxide band and of sulfone bands, again indicating the non-selectivity of the oxidation. Attempts to crystallize the oily material obtained by evaporating the chloroform failed.

Nitric Acid Oxidation.—The method was that used by Pollard and Robinson.[15] A solution of 3.02 g. (0.048 mole) of fuming nitric acid (d. 1.5) and 12.5 g. of acetic anhydride was added dropwise to a well-stirred solution of 19.5 g. (0.089 mole) of *m*-methylthiophenyl methanesulfonate in 50 g. of acetic anhydride. The addition was carried out at −20°, and the resulting green solution was allowed to stand at 0–5° for 24 hr. It was poured into ice-water, neutralized with sodium carbonate and extracted with chloroform. Evaporation of the chloroform and crystallization of the residue from methanol gave 19.1 g. (90%) of *m*-**methylsulfinylphenyl methanesulfonate** as white needles, m.p. 89–90°. An infrared analysis of this material did not reveal the presence of sulfone but showed a strong sulfoxide absorption band.

Anal. Calcd. for $C_8H_{10}O_4S_2$: C, 41.01; H, 4.30. Found: C, 40.88; H, 4.30.

m-Methylsulfinylphenyl methanesulfonate (17 g., 0.0078 mole) was stirred for 24 hr. at 50° in a solution made of 12 g. (0.4 mole) of sodium hydroxide pellets and 100 cc. of water. The clear solution was cooled, acidified with sulfuric acid, and the oil which was separated was extracted with chloroform. The chloroform was distilled and the residual oil was crystallized from chloroform–hexane to give 11.0 g. (83%) of a white, very hygroscopic material, m.p. 56–58°. Two additional recrystallizations from ether-hexane gave *m*-**hydroxyphenyl methyl sulfoxide** as long white needles, m.p. 61–62°. An infrared analysis showed that this material was free from sulfone.

Anal. Calcd. for $C_7H_8O_2S$: C, 53.82; H, 5.16; neut. equiv., 156.2. Found: C, 53.43; H, 5.11; neut. equiv., 155.0.

Benzoyl chloride was added to a basic solution of *m*-hydroxyphenyl methyl sulfoxide according to the Schotten–Baumann procedure described under *m*-hydroxyphenyl methyl sulfone. The oil obtained was crystallized thrice from hexane to give 69% yield of white plates, m.p. 91–92°. The absence of sulfone in the sample of *m*-**methylsulfinylphenyl benzoate** was confirmed by infrared analysis. Zincke and Ebel[5b] reported a m.p. of 84° for this material. It was found, however, that a 50% mixture of sulfoxide and sulfone melted between 81 and 86°.

Anal. Calcd. for $C_{14}H_{12}O_3S$: C, 64.55; H, 4.65. Found: C, 64.79; H, 4.73.

p-**Methoxyphenyl Methyl Sulfide.**—A solution of 0.57 g. (0.005 mole) of 30% hydrogen peroxide and 10 cc. of acetic anhydride was added to 0.77 g. (0.005 mole) of *p*-methoxyphenyl methyl sulfide in 10 cc. of acetic anhydride. The addition took place at −20 to −10°. The temperature was raised 30 minutes later to 0° for 4 hr. and to 10° for an additional 24 hr. After removal of the solvent under reduced pressure, the residual material was poured into a cold saturated solution of sodium bicarbonate and extracted with chloroform. Drying and concentration of this extract gave a yellowish oil which had an infrared spectrum identical to that of a pure sample of *p*-methoxyphenyl methyl sulfoxide.[22]

When this experiment was carried out at temperatures not exceeding 10–15°, infrared analysis showed the presence of only *p*-methoxyphenyl methyl sulfoxide; at higher temperatures, however, *p*-methoxyphenyl methyl sulfone, m.p. 120–121°, was isolated in appreciable quantity.

p-**Nitrophenyl Methyl Sulfide.**—Oxidation of *p*-nitrophenyl methyl sulfide with an equimolar amount of hydrogen peroxide in glacial acetic acid at 20–30° gave a product, m.p. 132–133°, which upon infrared analysis showed sulfoxide and sulfone bands. Additional recrystallizations did not lessen the amount of sulfone present. The oxidation of *p*-nitrophenyl methyl sulfide was effected according to the procedure of Pollard and Robinson,[15] *i.e.*, with fuming nitric acid in acetic anhydride at 0–10° for 24 hr. to give, after two recrystallizations from aqueous ethanol, 70% of a material, m.p. 152–153°. A melting point of 155° has been reported.[23] Infrared analysis showed only a sulfoxide peak.

A reaction mixture containing 0.74 g. (0.0066 mole) of 30% hydrogen peroxide and 1.0 g. (0.006 mole) of *p*-nitrophenyl methyl sulfide in 30 ml. of glacial acetic acid was divided into two equal parts; 0.46 g. (0.006 mole) of trifluoroacetic acid was added to one sample, and the solutions were allowed to stand at 25–30° for 72 hr. The solutions were then each poured into ice-water, neutralized with sodium carbonate and extracted with chloroform. The extracts were dried and after concentration on the steam-bath were placed directly in the cells of a Baird spectrophotometer. The sample to which trifluoroacetic acid had been added showed a strong sulfoxide band at 9.5 μ. The other sample showed the sulfoxide band, and also two weaker bands at 7.6 and 8.6 μ, which correspond to sulfone absorption bands.

TABLE III

ACIDITY CONSTANTS OF *m*- AND *p*-METHYLSULFINYLPHENOLS MEASURED IN WATER AT 25°

Substituent	C_a	C_b	*p*H	pK_a	pK_a(av.)
p-$CH_3S^+–O^-$	0.01890	0.00387	7.70	8.29	
	.09728	.00387	8.10	8.28	
	.01047	.00646	8.48	8.27	8.28
m-$CH_3S^+–O^-$	.01814	.00402	8.28	8.76	
	.02376	.00956	8.58	8.75	
	.02709	.01608	8.90	8.74	8.75

Acidity Constant Measurements.—Ionization constants for the phenols were determined in carbonate-free water with a Beckman model G *p*H meter standardized with Beckman buffers at *p*H 7 and 9. Calculations were made as described previously.[3d] The experimental results are given in Table III. We wish to thank Dr. Glenn D. Cooper for the ionization constants of the benzoic acids, which were determined as described previously.[3a]

EVANSTON, ILLINOIS

---

[22] Prepared from *p*-methoxyphenylmethylbromosulfonium bromide by hydrolysis (unpublished results).

[23] P. Oxley, W. W. Partridge, T. D. Robson and W. F. Short, *J. Chem. Soc.*, 863 (1946).