The reaction of *o*-bromofluorobenzene, magnesium and 1-pyrrolidinocyclohexene in refluxing ether for 2 days led to recovery of much *o*-bromofluorobenzene and magnesium and 0.40 g. of 2-phenylcyclohexanone but only a few mg. of pure picrate of XXXIX, from the basic fraction, together with a mixture of picrates, m.p. 105-166°.

Control.—Addition of 10.0 g. (0.066 mole) of 1-pyrrolidinocyclohexene to phenylmagnesium bromide, prepared from 17.0 g. (0.11 mole) of bromobenzene and 2.4 g. (0.10 g. atom) of magnesium, in 300 ml. of ether, gave 0.15 g. (1.3% yield) of 1-phenylcyclohexanol (derived from contaminating cyclohexanone), m.p. 61–62° (reported[44] 61°), in the neutral fraction and in the basic fraction 0.15 g. (1% yield) of crude 1-pyrrolidino-1-phenylcyclohexane, which formed 0.15 g. of picrate, m.p. 183–185°, after recrystallization from ethanol.

Anal. Calcd. for $C_{22}H_{26}N_4O_7$: C, 57.65; H, 5.74; N, 12.28. Found: C, 57.40; H, 5.98; N, 12.61.

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[44] P. Sabatier and A. Mailhe, *Compt. rend.*, **138**, 1321 (1904).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, VANDERBILT UNIVERSITY, NASHVILLE, TENN.]

Organic Disulfides and Related Substances. VI. A One-step Synthesis of Aromatic Sulfinic Esters from Lead Tetraacetate and Aromatic Disulfides or Thiols[1,2]

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Alkyl esters of variously substituted aromatic sulfinic acids were prepared, as well as representative heterocyclic and polynuclear esters. The novel and convenient one-step synthesis used was an oxidation of aromatic disulfides of thiols with lead tetraacetate in a mixture of chloroform and the appropriate alcohol. Primary, secondary or tertiary alcohols could be used. Steric effects of ring substituents reduced the yield much less than electron-withdrawing power. A sequence of reactions is advanced to account for the synthesis, and a modified value is offered for the molecular refraction constant of the sulfinoxy group, S(O)O–.

Relatively little is known of the action of lead tetraacetate on divalent organic sulfur compounds. It oxidizes sulfides specifically to sulfoxides, apparently in an ionic reaction[3]; thioanisole gives acetoxymethyl phenyl sulfide (43%), however, in addition to methyl phenyl sulfoxide (40%).[4] Although the reaction does not appear to proceed ordinarily to the most highly oxidized form of sulfur, oxidation of a sulfide to a sulfone has been reported (ruthenium dioxide catalysis).[5] With dibenzyl mercaptals of sugars, cleavage occurs and the principal sulfur-containing product is benzyl disulfide.[6]

In earlier work, we found that thiols could be oxidized conveniently to disulfides using lead tetraacetate.[7] With benzene or acetic acid as solvents, oxygenated derivatives of disulfides were not found, and use of lead tetraacetate thus provided an effective conversion for a variety of thiols to the disulfides. Despite this specificity of oxidation, however, it seemed quite likely that disulfides could be oxidized further under other conditions. Preliminary results showed that further oxidation did indeed occur in chloroform mixed with alcohols and that the reaction afforded a useful one-step preparation of sulfinic esters,[2] which hitherto have been difficultly obtainable. This paper elaborates upon and extends the preliminary observations.[2]

A reasonable equation for the over-all reaction seems to be

$$RSSR + 3Pb(OAc)_4 + 4R'OH \longrightarrow 2RS(O)OR' + 3Pb(OAc)_2 + 4AcOH + 2AcOR'$$

Thiols also can be used, owing to their facile oxidation to disulfides by lead tetraacetate.[7] In an attempt to substantiate the stoichiometry implicit in the equation, presumed lead diacetate and methyl acetate formed in one of the oxidations in chloroform–methanol (to compound VIII of Table I) were isolated. Based on the disulfide consumed, the product thought to be lead diacetate was found in three times the stoichiometry required by the above equation and the methyl acetate in more than four times the amount required. Evidently there is a substantial involvement of reactions other than that formulated, a result which is not really surprising in view of the excess amounts of both the tetraacetate and methanol which were used in this experiment.

The preparation of aromatic sulfinic esters from disulfides or thiols generally is superior to other known methods,[8,9] owing to the stability and ready availability of starting materials, the relatively attractive yields frequently obtained, the convenience of the process, and the fact that sulfonic esters (which usually are impurities in other routes) seem to be absent. Hopefully, the simplicity of this synthesis will lead to more extensive use and study of the interesting class of aromatic sulfinic esters.

Two general procedures were used in preparing the esters. In procedure A, lead tetraacetate (about four molar proportions) was added slowly to the disulfide in chloroform containing a large

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[1] Presented in part at the Southeastern Regional Meeting of the American Chemical Society at Birmingham, Ala., Nov. 3–5, 1960. Abstracted from portions of the Ph.D. dissertations of C.B.H., January, 1960, and J.M.L., January, 1962. Paper V, L. Field, W. D. Stephens and E. L. Lippert, Jr., *J. Org. Chem.*, **26**, 4782 (1961). Research supported by the U. S. Army Research Office, Durham, N. C.

[2] Preliminary account published by L. Field, C. B. Hoelzel, J. M. Locke and J. E. Lawson, *J. Am. Chem. Soc.*, **83**, 1256 (1961).

[3] H. E. Barron, G. W. K. Cavill, E. R. Cole, P. T. Gilham and D. H. Solomon, *Chemistry & Industry*, 76 (1954).

[4] L. Horner and E. Jürgens, *Ann.*, **602**, 135 (1957).

[5] M. Neeman and A. Modiano, Abstracts of the National A.C.S. Meeting at Miami, Fla., April 7–12, p. 83-O (1957).

[6] E. J. Bourne, W. M. Corbett, M. Stacey and R. Stephens, *Chemistry & Industry*, 106 (1954).

[7] L. Field and J. E. Lawson, *J. Am. Chem. Soc.*, **80**, 838 (1958).

[8] R. Connor in "Organic Chemistry. An Advanced Treatise," H. Gilman, Ed., Vol. I, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 916–917.

[9] F. Muth in "Methoden der Organischen Chemie (Houben-Weyl)," E. Müller, Ed., Vol. 9, 4th ed., G. Thieme Verlag, Stuttgart, 1955, pp. 338–340.

TABLE I

AROMATIC SULFINIC ESTERS PREPARED

			Total product					Carbon, %		Hydrogen, %		Sulfur, %		Molecular refraction	
No.	RS(O)OR′[a]	Procedure	Yield, %	Conversion, %	B.p., °C. (mm.)	$n^{25}\text{D}$ (m.p., °C.)	d^{25}_4	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
I	Phenyl	A	79	47	47.5–51[b] (0.2)	1.5434–7[b]	1.1927	53.82	53.57	5.16	5.37	20.53	20.74	41.46	41.32
		A′	62	38	53–66 (0.1)	1.5428–30									
II	2-Naphthyl	B[c]	33	33		(35–36.5)[c]		64.05	64.13	4.89	4.95	15.55	15.65		
III	2-Benzothiazolyl	A[d]	61	61		(72–74.5)[d]		45.05	45.13	3.31	3.58	30.07	30.26		
IV	Phenyl ($R' = n\text{-}C_3H_7$)	A[e]	87	61	75–102[e] (0.6–2.5)	1.5246–8[e]	1.1111	58.67	58.44	6.57	6.62	17.40	17.20	50.69	50.81
V	Phenyl ($R' = \text{iso-}C_3H_7$)	A[f]	80	38	110–117[f] (0.5)	1.5214–22[f]	1.1185	58.67	58.23	6.57	6.69	17.40	17.36	50.69	50.26
VI	2-Benzothiazolyl ($R' = (CH_3)_3C$)	B[g]	48	48		(52–63)[g]		51.74	51.57	5.13	5.48	25.11	25.28		
VII	o-Methoxycarbonylphenyl	B[h]	30	11[h]	111–115[h] (0.15)	1.5511–55[h]		50.46	49.18[h]	4.71	4.91	14.97	15.38	[h]	
VIII	*p*-Chlorophenyl	B	62	43	70–76[i] (0.2)	1.5618–27[i]		44.10	44.05	3.70	3.70	16.82	16.73	[i]	
IX	*o*-Tolyl	B′	72	72	66–71[j] (0.2)	1.5421–5[j]	1.1561	56.45	56.62	5.92	5.66	18.84	18.52	46.07	46.37
X	*p*-Tolyl	B[k]	73	73	60–65[k] (0.1)	1.5405–8[k]	1.1558	56.45	56.36	5.92	5.92	18.84	18.56	46.07	46.22
XI	2,6-Dimethylphenyl	B	79	79	95–98[l] (0.4)	1.5484–8[l] (12–12.5)	1.0955	58.67	58.74	6.57	6.75	17.40	17.59	50.69	53.45

[a] $R' = CH_3$, unless otherwise specified. [b] Reported (D. Barnard, *J. Chem. Soc.*, 4547 (1957): b.p. 55° (0.2 mm.), $n^{20}\text{D}$ 1.5440. [c] The final period of reflux after all additions of LTA completed was 24 hr. Crude II was extracted with hot pentane; chilling, finally on Dry Ice, gave first tar then II; II was recrystallized from pentane to constant m.p. 43–44° (m.p. reported, 42°; M. P. Balfe and W. G. Wright, *J. Chem. Soc.*, 1490 (1938). [d] Crude III recrystallized from methanol, isopropyl alcohol, cyclohexanone; constant m.p. 75.5–76°. [e] An equimolar amount of *n*-propyl alcohol was substituted for methanol in proc. A; pure IV had b.p. 90° (1.4 mm.), $n^{25}\text{D}$ 1.5248. [f] An equimolar amount of isopropyl alcohol was substituted for methanol in proc. A; difficulty was encountered in obtaining analytically pure material ($n^{25}\text{D}$ 1.5222). [g] An equimolar amount of *t*-butyl alcohol was substituted for methanol in proc. B. Crude VI was extracted with hot pentane; the extract was chilled in Dry Ice for *ca.* 72 hr.; solid was removed and recrystallized from pentane to constant m.p.; m.p. 77–78°. [h] Crude VII was extracted with hot pentane. The extract was cooled in ice, then Dry Ice; solid disulfide which formed was recrystallized from methanol; oil left after concentration of the pentane and methanol was distilled. Ester VII decomposed partly on distillation and evolved sulfur dioxide. Anal. sample: b.p. 114° (0.15 mm.), $n^{25}\text{D}$ 1.5516. [i] Pure VIII; b.p. 76° (0.2 mm.), $n^{25}\text{D}$ 1.5627; molecular refraction not determined owing to decomposition (1–2 days). [j] Pure IX: b.p. 66.5° (0.15 mm.), $n^{25}\text{D}$ 1.5424. [k] Kept at 25° instead of at reflux between the two additions of LTA. Reported by A. J. H. Houssa, J. Kenyon and H. Phillips, *J. Chem. Soc.*, 1700 (1929): $n^{20}\text{D}$ 1.5436, b.p. 82–85° (0.1 mm.). [l] Pure XI: b.p. 97° (0.4 mm.), $n^{25}\text{D}$ 1.5484.

excess of the appropriate alcohol. After a total period of reflux of about 24 hr., the organic layer was washed with water and the sulfinic ester then was purified by distillation or recrystallization. Procedure B differs from A in that the treatment with lead tetraacetate was repeated in order to increase the yield somewhat at the expense of significant amounts of disulfide which often are recovered in procedure A. Procedure A seems the method of choice where the disulfide is less expensive than the tetraacetate and where it can be separated easily; procedure B would be preferable in the converse situation. Procedures A′ and B′ differ from their counterparts A and B in that the thiol is used as the starting material.

In order to determine the generality and characteristics of the synthesis, the eleven sulfinic esters shown in Table I were prepared. Methyl benzenesulfinate (I) was obtained satisfactorily from either phenyl disulfide or thiophenol. Synthesis of methyl 2-naphthalenesulfinate (II) and of methyl 2-benzothiazolesulfinate (III) show that the procedure can be used with a polynuclear or heterocyclic system.

In most instances, the alkyl radical was methyl, but other esters also could be prepared. It has long been known that esters of sulfinic acids other than ethyl esters can be prepared from the ethyl esters by ester interchange.[10] With the object of preparing other esters in one step, however, equimolar amounts of *n*-propyl alcohol and of isopropyl alcohol were substituted for methanol in the oxidation of phenyl disulfide. The corresponding *n*-propyl (IV) and isopropyl (V) esters of benzenesulfinic acid resulted. Attempts to substitute *t*-butyl alcohol for methanol in the same reaction apparently gave the crude ester in good yield, as suggested by infrared spectroscopy,[11] but attempts to distil the ester resulted in decomposition at about 70° under reduced pressure. Since methyl 2-benzothiazolesulfinate (III) was a solid, it seemed probable that the *t*-butyl ester might also be solid and therefore amenable to purification under mild conditions. Treatment of 2-benzothiazolyl disulfide with lead tetraacetate in chloroform containing *t*-butyl alcohol justified this expectation and yielded the solid *t*-butyl ester (VI).

The possibility of substituting an unsaturated alcohol for methanol failed when allyl alcohol was used with phenyl disulfide. Instead of the known allyl benzenesulfinate, a liquid resulted which contained no sulfur, and phenyl disulfide was recovered in 88% yield. The liquid seemed to be an unsaturated ester but was not investigated further. Evidently the tetraacetate attacked the unsaturated alcohol in preference to the disulfide, a result which is not surprising since it will acetoxylate a carbon–carbon double bond.[12]

An attempt was made to oxidize *o*-nitrophenyl disulfide to methyl *o*-nitrobenzenesulfinate in order to determine the effect of an electron-withdrawing

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[10] H. Phillips, *J. Chem. Soc.*, **127**, 2552 (1925).

[11] S. Detoni and D. Hadži, *ibid.*, 3163 (1955).

[12] *Cf.* R. Criegee, *Angew. Chem.*, **70**, 173 (1958).

substituent; the disulfide was recovered in 92% yield. When *p*-nitrophenyl disulfide was subjected to the same conditions, it was recovered in 78% yield, although characteristic peaks in the infrared spectrum[11] indicated that a trace of methyl *p*-nitrobenzenesulfinate also had been formed. Although the failure with the *o*-nitro isomer could be explained by either a steric or electron-withdrawing effect of the *o*-nitro group, the poor result with the *p*-nitro isomer strongly implies that electron withdrawal is far more significant in conferring resistance to the oxidation. This conclusion is substantiated by the relatively low conversion of *o*-methoxycarbonylphenyl disulfide to the sulfinic ester VII. The only product isolated when pentachlorobenzenethiol was subjected to procedure B′ was the disulfide (46%), but methyl *p*-chlorobenzenesulfinate (VIII) was obtained satisfactorily from the corresponding disulfide (although in somewhat low conversion).

A surprising degree of insensitivity to steric hindrance in the oxidation was foreshadowed by the similarity in yields of methyl *o*-toluenesulfinate (IX, 72%) and of methyl *p*-toluenesulfinate (X, 73%). This relative insensitivity was confirmed by preparation of methyl 2,6-dimethylbenzenesulfinate (XI) in 79% yield from 2,6-dimethylphenyl disulfide.

Evidence that the products reported in Table I have the assigned structures was afforded by: (a) Elemental analysis. (b) Strong infrared absorption at 1099–1153 and 889–990 cm.$^{-1}$. Absorption at 1126–1136 and 960 cm.$^{-1}$ is reported to be characteristic for aromatic sulfinic esters.[11] Comparison of the spectra of I, II and X with reported spectra established the identity of these three esters beyond question.[13] (c) Molecular refraction: The values listed as "Found" in Table I were calculated as usual from the density and refractive index. "Calcd." values were obtained using the value of 10.53 (±0.2) for the sulfinoxy group, –S(O)O–, instead of 11.05 which has been suggested.[14] (d) Saponification equivalent of I (calcd. 156, found 153): The presence of the sulfinoxy moiety was assured by conversion of the resulting sodium benzenesulfinate to phenyl 2,4-dinitrophenyl sulfone in 52% yield.[16]

The liquid sulfinic esters were rather reactive in that they underwent rapid hydrolysis to the sulfinic acid upon standing in air at room temperature. Hydrolysis was followed by fairly rapid oxidation of the sulfinic to the sulfonic acid. Benzenesulfinic acid which formed thus from methyl benzenesulfinate (I) was identified as its *p*-toluidine salt, and the sulfonic acid which formed on continued exposure to air also was identified as its *p*-toluidine salt. In consequence of the hydrolysis and oxidation, when Compound I was exposed to air it solidified in about 5 hr. (formation of the sulfinic acid) and after 24 hr. more had again become liquid (formation of the hygroscopic sulfonic acid). In contrast to the behavior of the liquid esters, solid esters could be handled in air and generally seemed stable (at least at 5°) over periods of several months.

A sequence of equations can be formulated for the reaction of organic disulfides with lead tetraacetate in a mixture of chloroform and an alcohol, which affords an explanation as to how sulfinic esters may be formed. This sequence was suggested by views of Levitt on oxidation[17] and of Criegee[12] and Mosher and Kehr[18] on species involved in reactions of the tetraacetate. It encompasses the five steps which follow

$$\mathrm{Pb(OAc)_4} \longrightarrow \mathrm{Pb(OAc)_2} + \mathrm{AcO^+} + \mathrm{AcO^-} \quad (1)$$

Modification of step 1 would be more consonant with views expressed by Criegee (*i.e.*, $\mathrm{Pb(OAc)_4} \rightarrow \mathrm{Pb(OAc)_3^+} + \mathrm{AcO^-}$), but for present purposes the lead triacetate cation preferred by Criegee is essentially equivalent to the acetoxonium ion mentioned by Mosher and Kehr[18] and Barron and coworkers.[3]

$$\mathrm{RSSR} + \mathrm{AcO^+} \longrightarrow \mathrm{R\overset{+}{S}(OAc)SR} \quad (2)$$

The likelihood that a cationic species, such as the acetoxonium ion, attacks the disulfide is indicated by the remarks already made regarding the resistance to oxidation which develops when electron-withdrawing substituents are present on the ring. At this juncture, however, the assumption would be unwise that the oxidation *necessarily* proceeds by a heterolytic pathway instead of a homolytic one; indeed, isolation of hexachloroethane in the attempted oxidation of *p*-nitrophenyl disulfide strongly suggests that free radicals are present in the reaction, at least to some extent.

$$\mathrm{R\overset{+}{S}(OAc)SR} \longrightarrow \mathrm{RS(O)SR} + \mathrm{Ac^+} \quad (3)\,(a)$$

$$\mathrm{Ac^+} + \mathrm{CH_3OH} \longrightarrow \mathrm{AcOCH_3} + \mathrm{H^+} \quad (b)$$

It seems quite likely that steps 3a and 3b would be concerted, but speculation is unwarranted on possible variations in detail of this kind.

$$\mathrm{RS(O)SR} + \mathrm{CH_3OH} \overset{\mathrm{H^+}}{\rightleftarrows} \mathrm{RS(O)OCH_3} + \mathrm{RSH} \quad (4)\,(a)$$

To test the possibility that a thiolsulfinate ester is an intermediate, eq. 4a, the exchange reaction between phenyl benzenethiolsulfinate—prepared by oxidation of phenyl disulfide with perbenzoic

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(13) Cards 1061–1063, respectively, in the collection published by Butterworths (London) and Verlag Chemie (Weinheim), Dec., 1956. The spectrum of our I lacked bands at 1370 and 1185 cm.$^{-1}$ present in the published spectrum; these evidently resulted from methyl benzenesulfonate, which absorbs strongly at these points.

(14) The value of 11.05 was proposed by R. Boudet and R. Rambaud, *Bull. soc. chim. France*, **15**, 793 (1948). This value at first was used with other conventional ones,[15] but the calcd. value for the molecular refraction which resulted was consistently higher than that found experimentally. Accordingly, for each of the compounds I, IV, V, IX and X, the sum of all group refractions[15] except for –S(O)O– were subtracted from the "Found" values of Table I; an average of the differences gave the new value of 10.53 ± 0.2 for the sulfinoxy group. This new value was used in obtaining all "Calcd." values of Table I. The exaltation of molecular refraction for XI was so great, despite its purity as evidenced by analysis, that XI was not used in obtaining the new value for the refraction of the sulfinoxy group.

(15) J. A. Leermakers and A. Weissberger in "Organic Chemistry. An Advanced Treatise," H. Gilman, Ed., Vol. II, 2nd ed., John Wiley and Sons, Inc., New York, 1943, p. 1751.

(16) Procedure of M. S. Kharasch, E. M. May and F. R. Mayo, *J. Org. Chem.*, **3**, 190 (1938); m.p. 159–161°; reported m.p. 161° (R. W. Bost, J. O. Turner and R. D. Norton, *J. Am. Chem. Soc.*, **54**, 1985 (1932)).

(17) L. S. Levitt, *J. Org. Chem.*, **20**, 1297 (1955).

(18) W. A. Mosher and C. L. Kehr, *J. Am. Chem. Soc.*, **82**, 5342 (1960).

acid[19]—was attempted in the presence of acetic acid. Removal of volatiles under reduced pressure left only a gray solid, which was not studied further, instead of the liquid sulfinate I. A possible explanation lies in the observation that thiolsulfinates decompose rapidly under reduced pressure according to the equation $2RS(O)SR \rightarrow RSO_2SR + RSSR$.[20] The fact that substitution of phenyl benzenethiolsulfinate for phenyl disulfide in the preparation of I by procedure B resulted in formation of I in 53% yield supports the view that the thiolsulfinate may indeed be an intermediate; possibly the exchange occurs only in the presence of lead tetraacetate because completion of the reaction requires oxidation of the thiol to the disulfide, step 4b.[7]

On the other hand, a referee suggested that the thiolsulfinate might behave as a sulfenyl derivative; as such it might react with alcohols in several ways, one perhaps being by attack upon the RS– moiety to give a sulfenate ($RSOCH_3$) which upon subsequent oxidation might yield a sulfinate. We share the referee's opinion that only cautious and preliminary suggestions as to the nature of reactions of the thiolsulfinate are warranted at present and, indeed, would emphasize this viewpoint for all of the reactions 1–5 which are mentioned.

$$2RSH + Pb(OAc)_4 \longrightarrow RSSR + Pb(OAc)_2 + 2AcOH \quad (4)\,(b)$$

$$AcO^- + H^+ \longrightarrow AcOH \quad (5)$$

Experimental[21]

The source, assay, etc., of lead tetraacetate (LTA) were as previously described.[7] Disulfides were prepared by oxidation of thiols with bromine[22] or LTA,[7] or were recrystallized commercial products. 2,6-Dimethylphenyl disulfide was prepared from 2,6-dimethylaniline.[23]

Preparation of Sulfinic Esters. Procedure A.—The general method may be illustrated as follows: A solution of LTA (0.29–0.30 mole) in chloroform (550–600 ml.) was added to a stirred mixture of disulfide (0.075 mole) in 140 ml. of chloroform and 140 ml. of methanol at the reflux temperature during 8.5–12 hr. The mixture was kept at the reflux temperature for about 12 hr. and then was cooled. Water (100 ml.) was added to decompose any residual LTA and the entire mixture then was filtered through a Celite-coated filter paper to remove lead dioxide. The chloroform layer was washed with distilled water until the washings were free from lead ions (no precipitate with aqueous sodium sulfide). The chloroform solution then was dried over anhydrous magnesium sulfate and, after separation of the drying agent, was concentrated at room temperature by means of a rotating-flask evaporator. Distillation of liquids was effected with 21–47 cm. spinning-band columns (Nester and Faust, Wilmington, Del.) at the pressures indicated in Table I. Solids were purified as described in footnotes to Table I.

Procedure B.—Procedure B differs from A chiefly in that after the first addition of LTA and the subsequent heating period were complete, the addition and heating were repeated. The disulfide was used in chloroform (140–600 ml.)—methanol (75, usually-140 ml.) with LTA (0.30–0.34 mole) in chloroform (550–600 ml.). After the heating period of 10–24 hr. (usually 12 hr.), the addition of LTA (11 hr.) was repeated, as was heating under reflux (8.5–12 hr.). The mixture then was cooled. Products were isolated as described in procedure A.

Procedures A′ and B′.—The thiol (0.15 mole) in chloroform (50–100 ml.) first was oxidized to disulfide by addition to 0.093 mole of LTA in 500 ml. of chloroform during about 1 hr. at about 25°. Procedure A or B then was followed, except that owing to the chloroform already present the amount ordinarily used to dissolve the disulfide was omitted.

Conversion of Phenyl Benzenethiolsulfinate to Methyl Benzenesulfinate (I).—Phenyl benzenethiolsulfinate[19] (m.p. 68.5–69.5°, reported[19] 69°) was submitted to procedure B, with the thiolsulfinate being substituted for the same molar proportion of phenyl disulfide usually used. Thus, the thiolsulfinate (1.47 g., 6.3 mmoles) in chloroform (15 ml.) and methanol (6.3 ml.) was heated to the reflux temperature, and LTA (28 mmoles) in chloroform (50 ml.) was added during 11 hr. The initially yellow solution darkened immediately on addition of the LTA solution. After completion of addition, as usual the mixture was kept at the reflux temperature for 12 hr., another portion of LTA added (28 mmoles) in chlofororm (50 ml.) during an additional 11 hr., and the mixture kept at reflux for 12 hr. more. The mixture was cooled, water (16 ml.) added, and the product isolated as usual. Removal of the chloroform left 1.86 g. of yellow oil, 1.70 g. of which was distilled using a 47-cm. spinning-band column to give 0.948 g. (53%) of I, b.p. 55–56° (0.25 mm.), $n^{25}D$ 1.5434–1.5436. The infrared spectrum of the I was identical with that of other samples prepared earlier.

Preparation of Methyl *p*-Chlorobenzenesulfinate with Isolation of Lead Diacetate and Methyl Acetate.—*p*-Chlorophenyl disulfide (5.39 g., 19 mmoles) in chloroform (35 ml.) and methanol (19 ml.) was heated to the reflux temperature and, according to procedure B, 85 mmoles of LTA in chloroform (150 ml.) was added (11 hr.). After 12 hr. under reflux, addition of 85 mmoles of LTA as before, and stirring for 12 hr., the cooled mixture was treated with water (25 ml.) and filtered. The chloroform–water filtrate was chilled at 8° for 8 hr. to allow precipitation of lead diacetate. When precipitation seemed complete, the presumed lead diacetate was collected, dried and weighed; the possibility of variously hydrated and basic forms obviated identification by X-ray diffraction. The weight was 38.90 g.; assuming the solid to be anhydrous lead diacetate, the yield was about three times the theoretical amount, based on unrecovered disulfide.

The chloroform solution then was washed with water and dried. The solution was concentrated to an oil (6.83 g.), condensate being collected in a trap chilled with Dry Ice–acetone. The oil (6.13 g.) was distilled through a 47-cm. spinning-band column; residue was recrystallized from ethanol and gave 1.61 g. of *p*-chlorophenyl disulfide (30% recovery), m.p. and mixture m.p. 71–72°. There resulted 2.78 g. (62%) of pure VIII with the properties reported in Table I.

The chloroform solution of methyl acetate (566 g.) which collected in the trap was dried over magnesium sulfate. Its infrared spectrum contained all the bands of chloroform and methyl acetate, but no others. By comparing the absorbance at 1736 cm.$^{-1}$ with samples containing known amounts of methyl acetate in chloroform, the solution was found to contain 1.5% of methyl acetate (4.4 times the theoretical amount).

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(19) P. L. N. Rao and S. C. L. Verma, *J. Indian Inst. Sci.*, **34**, 315 (1952); *C. A.*, **47**, 9290 (1953).

(20) D. Barnard, *J. Chem. Soc.*, 4675 (1957).

(21) Melting points are corrected and boiling points are uncorrected. Analyses are by Galbraith Microanalytical Laboratory, Knoxville, Tenn., and L. Haynes, Nashville, Tenn. Infrared spectra were determined using a model 137 Perkin–Elmer spectrophotometer usually with neat liquids or Nujol mulls.

(22) L. Field and F. A. Grunwald, *J. Org. Chem.*, **16**, 946 (1951).

(23) J. R. Cox, Jr., C. L. Gladys, L. Field and D. E. Pearson, *ibid.*, **25**, 1083 (1960).