EXPERIMENTAL

The isomerization of 4-biphenylyl benzenesulfonate. A mixture of 5 g. (0.016 mole) of 4-biphenylyl benzenesulfonate and 7.2 g. (0.054 mole) of powdered anhydrous aluminum chloride was heated at 140–160° for 1 hr. After cooling, the product was decomposed with ice and hydrochloric acid. The resulting solid was filtered and extracted with dilute sodium hydroxide solution. The alkali extract was acidified, filtered, and extracted with ether. Evaporation of ether gave 0.15 g. (3%) of a product which, on repeated crystallization from ethanol, melted at 97–99°. The melting point was not depressed on admixture with *4-hydroxy-3-phenylsulfonylbiphenyl*, synthesized unambiguously.

Anal. Calcd. for $C_{18}H_{14}O_3S$: C, 69.65; H, 4.54. Found: C, 69.50; H, 4.42.

4-Methoxy-3-phenylthiobiphenyl. To a solution of sodium ethoxide (0.7 g. of sodium in 10 ml. of absolute ethanol) 3.3 g. (0.03 mole) of thiophenol was added and the alcohol was evaporated. The resulting phenyl sodium sulfide was mixed with 8 g. (0.03 mole) of 3-bromo-4-methoxybiphenyl[2] and 0.8 g. of copper powder and heated at 220–240° for 4.5 hr. After cooling, the product was treated with 3 g. of zinc dust and 100 ml. of dilute (2*N*) sulfuric acid and steam-distilled. Extraction of the residue with ether gave the *sulfide*. The yield was 8 g. (90%). It boiled at 220–223°/6 mm. and was obtained as a viscous liquid.

Anal. Calcd. for $C_{19}H_{16}OS$: C, 78.03; H, 5.52. Found: C, 78.30; H, 5.60.

4-Methoxy-3-phenylsulfonylbiphenyl. A solution of 3 g. of the foregoing sulfide in glacial acetic acid was treated with excess of saturated potassium permanganate solution and heated on a water bath for 15 min. The solution was then decolorized with sulfur dioxide, diluted with water, and the precipitated solid was filtered. Crystallization from ethanol gave 2.1 g. (63%) of the *sulfone;* m.p. 177–179°.

Anal. Calcd. for $C_{19}H_{16}O_3S$: C, 70.36; H, 4.97. Found: C, 70.41; H, 5.00.

4-Hydroxy-3-phenylsulfonylbiphenyl. A mixture of 1 g. of the above sulfone and 10 ml. of hydriodic acid (*d* 1.7) was heated at 160–170° for 5 hr. The product was poured into water, the precipitated solid was removed by filtration, washed with water and extracted with dilute sodium hydroxide solution. Acidification of the alkali extract gave an oil which solidified slowly. The yield was 0.6 g. (63%). The compound was crystallized from ethanol; m.p. 97–99°.

Anal. Calcd. for $C_{18}H_{14}O_3S$: C, 69.65; H, 4.54. Found: C, 69.39; H, 4.40.

Isomerization of 4-biphenylyl-p-toluenesulfonate. The procedure was the same as that described for the benzenesulfonate. The yield of the hydroxy sulfone was 8%. After recrystallizing from ethanol, it melted at 112–114°. There was no depression in the melting point on admixture with *4-hydroxy-3-p-tolylsulfonylbiphenyl*, synthesized unequivocally.

Anal. Calcd. for $C_{19}H_{16}O_3S$: C, 70.36; H, 4.97. Found: C, C, 70.57; H, 5.01.

4-Methoxy-3-p-tolylthiobiphenyl was obtained from 3-bromo-4-methoxydiphenyl and *p*-thiocresol in 79% yield. It boiled at 258–260°/9 mm.

Anal. Calcd. for $C_{20}H_{18}OS$: C, 78.39; H, 5.92. Found: C, 78.59; H, 5.99.

4-Methoxy-3-p-tolylsulfonylbiphenyl. Oxidation of the above sulfide with potassium permanganate solution gave this *sulfone* in 60% yield. It was crystallized from ethanol; m.p. 171–173°.

Anal. Calcd. for $C_{20}H_{18}O_3S$: C, 70.99; H, 5.36. Found: C, 71.01; H, 5.40.

4-Hydroxy-3-p-tolylsulfonylbiphenyl was obtained in 60% yield by demethylating the foregoing compound with hydriodic acid. After recrystallizing from ethanol, it melted at 112–114°.

Anal. Calcd. for $C_{19}H_{16}O_3S$: C, 70.36; H, 4.97. Found: C, 70.15; H, 4.79.

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[2] D. H. Hey and E. R. B. Jackson, *J. Chem. Soc.*, 802 (1936).

The Reactions of Thiolsulfonates and Thiolsulfinates with 1-Fluoro-2,4-dinitrobenzene

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Leandri and Tundo[1] have shown that 2,4-dinitrochlorobenzene reacts with aromatic thiolsulfonates to yield the corresponding 2,4-dinitrophenyl sulfones. We have studied this reaction employing the more reactive 1-fluoro-2,4-dinitrobenzene at room temperature in the attempt to develop methods for characterizing thiolsulfonates (RSO_2SR') and thiolsulfinates (RSO—SR′) and mixtures of the two. Thiolsulfonates and thiolsulfinates reacted with excess fluorodinitrobenzene at 25° for forty to sixty hours in aqueous acetone–sodium bicarbonate suspension, aqueous tetrahydrofuran–sodium bicarbonate suspension, or in dimethylformamide–water–triethylamine solution and the products were separated by direct crystallization and by adsorption chromatography.

p-Tolyl *p*-toluenethiolsulfonate yielded, in addition to the expected 2,4-dinitrophenyl *p*-tolyl sulfone (65–89%), 2,4-dinitrophenyl *p*-tolyl sulfoxide (7–9%) and smaller yields of the corresponding sulfide.

The isolation of sulfoxide in these reactions is evidence that, in addition to reaction of the RSO_2 moiety with fluorodinitrobenzene to yield sulfone, the RS portion of the thiolsulfonate must yield the unstable intermediate sulfenic acid [RSOH] which reacts with fluorodinitrobenzene to give sulfoxide. The sulfenic acid may result either from a concerted reaction in which RS is eliminated as RSF which is hydrolyzed to sulfenic acid or from a direct reaction of hydroxyl ion on the positively polarized RS of the reacting molecule or on separated RS^+.[2] More convincing evidence for this was obtained

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[1] G. Leandri and A. Tundo, *Ann. Chim.* (*Rome*), **44**, 255, 264 (1954).

[2] The chemistry of the sulfenic acids has been summarized by Kharasch: N. Kharasch, S. J. Potempa, and H. Wehrmeister, *Chem. Revs.*, 39, 269 (1946); N. Kharasch, "The Sulfenic Acids and their Derivatives," in *Organic Sulfur Compounds*, Vol. I, Pergamon Press, London (1959).

from the reaction of methyl methanethiolsulfonate with fluorodinitrobenzene in which case the 2,4-dinitrophenyl methyl sulfone was isolated in a yield greater than that calculated if it were formed from the methanesulfonyl group alone and the corresponding sulfoxide was obtained in a 12% yield. The isolation of sulfone in amounts in excess of that calculated is probably due to disproportionation of the intermediate sulfenic acid $2\ RSOH \rightarrow RSH + RSO_2H$ followed by reaction of the sulfinic acid with fluorodinitrobenzene to yield additional sulfone and conversion of the thiol to the dinitrophenyl sulfide.

Fromm and de Seixas Palma[3] showed that benzyl benzylthiolsulfonate on refluxing with alcoholic sodium hydroxide and benzyl chloride yielded not only dibenzyl sulfone but also the sulfoxide. An intermediate sulfenic acid was postulated to explain the formation of sulfoxide. However, Fromm[4] was unable to isolate sulfoxide when *p*-tolyl *p*-toluenethiolsulfonate was used although the corresponding sulfone was obtained. The present work shows that the formation of an intermediate sulfenic acid probably occurs also with a typical aromatic and an aliphatic thiolsulfonate under mild conditions of temperature and alkalinity.

It would be anticipated that reaction of thiolsulfinates with fluorodinitrobenzene would yield the corresponding dinitrophenyl sulfoxide not only from the RSO moiety but also from RS through the sulfenic acid. *p*-Tolyl *p*-toluenethiolsulfinate with fluorodinitrobenzene in dimethylformamide containing water and triethylamine, however, yielded only 29% of the sulfoxide with 46% of sulfone and 15% of sulfide. With aqueous acetone and sodium bicarbonate, yields were even lower. With aliphatic thiolsulfinates, yields of sulfoxide and sulfone were also lower. Yields were not improved when thiolsulfinates were refluxed with 2,4-dinitrochlorobenzene in aqueous ethanol containing sodium bicarbonate or sodium carbonate.

Chromatography on silicic acid containing fluorescent zinc sulfide was particularly useful for separating sulfoxides and sulfides from sulfones, the general rate of movement being sulfide > sulfone > sulfoxide. Dinitrophenyl sulfides and sulfoxides appeared as yellow bands while the sulfones, colorless by visible light, could be observed by the quenching of fluorescence in the ultraviolet.

These results show that reaction with fluorodinitrobenzene is not generally a satisfactory procedure for characterizing unsymmetrical thiolsulfonates and particularly thiolsulfinates.

EXPERIMENTAL

p-Tolyl p-toluenethiolsulfinate was prepared as described previously,[5] dec. 102°. Absence of thiolsulfonate was established by infrared (potassium bromide pellet), strong absorption at 1090 cm.$^{-1}$ (characteristic for $\overset{\text{O}}{\overset{|}{\text{S}}}\text{—S}$)[6] and no absorption at 1140 cm.$^{-1}$ (SO_2 absorption in thiolsulfonates).

p-Tolyl p-toluenethiolsulfonate was prepared by thermal decomposition of the thiolsulfinate, m.p. 77–78°. Infrared showed strong absorption at 1140 cm.$^{-1}$ with no absorption at 1090 cm.$^{-1}$ (absence of thiolsulfinate).

Methyl methanethiolsulfonate was prepared by oxidation of methyl disulfide with 30% hydrogen peroxide in chloroform solution and the compound was purified by short-path vacuum distillation (0.05 mm.). Purity and particularly freedom from thiolsulfinate was established by infrared (liquid), absorption at 1430 (weak), 1330 (strong), 1300 (strong), 1134 (strong), 960 (strong), and 748 cm.$^{-1}$ (strong) substantially in agreement with Ostermayer and Tarbell.[7]

Reaction of p-tolyl p-toluenethiolsulfonate with 1-fluoro-2,4-dinitrobenzene. A solution containing 1.00 g. (0.00359 mole) of *p*-tolyl *p*-toluenethiolsulfonate and 2.5 g. (0.0136 mole) of fluorodinitrobenzene in 80 ml. of dimethylformamide containing 8 ml. of triethylamine and 4 ml. of water was allowed to react under nitrogen for 44 hr. at room temperature. The deep amber solution was concentrated *in vacuo* to *ca.* 10 ml. which was dissolved in 300 ml. of chloroform and extracted twice with 150-ml. portions of 5% aqueous sodium carbonate. Evaporation of the chloroform yielded a solid residue from which 1.0 g. (86%) of 2,4-dinitrophenyl *p*-tolyl sulfone was obtained as colorless plates by crystallization from ethanol, m.p. 187–189°, melting undepressed when mixed with the authentic compound. The infrared spectrum (potassium bromide pellet) was identical with that of the authentic compound.

The mother liquor, after removal of sulfone, was dissolved in 50 ml. of benzene and adsorbed on a column of silicic acid–zinc sulfide (1%), 48 × 220 mm. The chromatogram was developed with hexane–ethyl acetate (20:1) and a rapidly moving yellow band was eluted to give 48 mg. (4%) of 2,4-dinitrophenyl *p*-tolyl sulfide, m.p. 102–103°, undepressed when mixed with the authentic compound. Development with 2850 ml. of solvent yielded a pale yellow band 1 cm. below the top and a second band, colorless in daylight but strongly quenching fluorescence in the ultraviolet, just below the upper band. The colorless band when carved out and extracted with ethyl acetate yielded 33 mg. (3%) of 2,4-dinitrophenyl *p*-tolyl sulfone. The slower moving yellow band yielded 82 mg. (7%) of 2,4-dinitrophenyl *p*-tolyl sulfoxide obtained by recrystallization from ethanol as yellow plates, m.p. 136–137° undepressed when mixed with an authentic sample.

Anal. Calcd. for $C_{13}H_{10}N_2SO_5$, C, 50.98; H, 3.29; S, 10.47. Found, C, 51.1; H, 3.42; S, 10.7.

In the infrared (potassium bromide pellet), the compound had a strong sulfoxide band at 1060 cm.$^{-1}$ and no absorption at 1140–1170 cm.$^{-1}$

In a second experiment, 2.0 g. of *p*-tolyl *p*-toluenethiolsulfonate, 5.0 g. of fluorodinitrobenzene and 9 g. of sodium bicarbonate in suspension in 250 ml. of acetone and 50 ml. of water were stirred magnetically under nitrogen for 40 hr. at room temperature to give a 65% yield of sulfone and a 9.4% yield of sulfoxide.

Reaction of methyl methanethiolsulfonate with 1-fluoro-2,4-dinitrobenzene. A mixture of 1.34 g. (0.0106 mole) of methyl methanethiolsulfonate, 5.0 g. (0.0272 mole) of fluorodinitrobenzene and 7.0 g. of sodium bicarbonate in 100 ml. of tetrahydrofuran and 50 ml. of water was stirred under nitrogen for 47 hr. at 25°. The deep yellow suspension was filtered and the white solid washed with 500 ml. of water to remove

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(3) Emil Fromm and Jose de Seixas Palma, *Ber.*, **39**, 3308 (1906).

(4) Emil Fromm, *Ber.*, **41**, 3397 (1908).

(5) J. F. Carson and Francis F. Wong, *J. Org. Chem.*, 26, 1467(1961)..

(6) D. Barnard, *J. Chem. Soc.*, 4673 (1957).

(7) F. Ostermayer and D. S. Tarbell, *J. Am. Chem. Soc.*, 82, 3752 (1960).

bicarbonate and salts. Recrystallization of the solid precipitate from ethanol–ethyl acetate yielded 1.87 g. of colorless needles, m.p. 186–187°. This was identified as 2,4-dinitrophenyl methyl sulfone by mixed melting point with authentic material and infrared (potassium bromide pellet) showing strong absorption at 1155 cm.$^{-1}$ and no absorption between 1040 and 1090 cm.$^{-1}$

The aqueous tetrahydrofuran solution on concentration *in vacuo* to dryness yielded additional solid from which 0.85 g. of pure sulfone was isolated. The combined yield of sulfone by direct crystallization was 2.72 g. (104%).

The mother liquor from these two fractions was stripped of solvent *in vacuo* and the residual solid dissolved in benzene and adsorbed on a 48 × 300 mm. column of silicic acid–zinc sulfide 1%. Development with 4500 ml. of hexane–ethyl acetate (12:1) yielded a sharp yellow band 2 cm. from the top and a second colorless (quenching fluorescence) band just below. The upper band was carved out and extracted with ethyl acetate to yield 0.303 g. of 2,4-dinitrophenyl methyl sulfoxide (12%) as canary yellow plates, m.p. 165–166.4°.

Anal. Calcd. for $C_7H_6N_2SO_5$: C, 36.52; H, 2.6; S, 13.93. Found: C, 36.7; H, 2.67; S, 14.2.

It was further identified by mixed melting point and by infrared (potassium bromide pellet), strong adsorption at 1060 cm.$^{-1}$ (sulfoxide) and no absorption at 1160 cm.$^{-1}$ (sulfone).

The lower colorless band on extraction with ethyl acetate gave 95 mg. (3%) of 2,4-dinitrophenyl methyl sulfone to give a combined yield of 107% sulfone.

p-Tolyl p-toluenethiolsulfinate and fluorodinitrobenzene. A solution of 0.8 g. (.00305 mole) of *p*-tolyl *p*-toluenethiolsulfinate and 2.5 g. (0.0136 mole) of fluorodinitrobenzene in 80 ml. of dimethylformamide containing 5 ml. of triethylamine and 5 ml. of water was allowed to react for 36 hr. at 25°. The deep amber solution was concentrated *in vacuo* to an oil (*ca.* 20 ml.) which was dissolved in 250 ml. of chloroform. The chloroform solution was extracted with 100 ml. of 5% aqueous sodium carbonate solution, dried over sodium sulfate and again reduced to an oil *in vacuo.* Crystallization from ethanol yielded 0.46 g. (47%) of 2,4-dinitrophenyl *p*-tolyl sulfone as colorless micaceous plates and the mother liquor yielded 0.24 g. (26%) of the sulfoxide as yellow prisms, mp. 136–137°. The mother liquor from these two crops when chromatographed on silicic acid and developed as previously described yielded 0.132 g. (15%) of 2,4-dinitro-phenyl *p*-tolyl sulfide as lemon yellow coarse prisms and 0.033 g. (3.5%) of the sulfoxide.

When the thiolsulfinate reacted with fluorodinitrobenzene in aqueous acetone-bicarbonate or aqueous ethanol-bicarbonate for periods of time varying from 36–65 hr., yields of sulfoxide were generally 19–24%, and sulfone, 10–15%.

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Preparation of Alkyl Thioborates

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Only a few examples of alkyl thioborates, $(RS)_3B$, have been described in the literature. The only reported methods for the preparation of alkyl thioborates are the reactions of boron tribromide with lead,[1] silver,[1] or sodium mercaptides,[2] the disproportionation of methylthioborine polymers $(CH_3SBH_2)_n$;[2] and the reaction of trimethylamine borane with *n*-butyl or *n*-amyl mercaptan.[3] We would now like to report the development of more direct methods for preparing alkyl thioborates from either boron trihalides or tris(amino)boranes.

Pure thioborates could not be obtained conveniently by the direct displacement of amines from tris(amino)boranes by mercaptans. However, when the reaction of methyl mercaptan with tris(dimethylamino)borane was carried out at low temperatures in the presence of three molar equivalents of anhydrous hydrogen chloride in ether as shown, a 51.8% yield of the desired product was obtained.

$$B[N(CH_3)_2]_3 + 3\ CH_3SH + 3\ HCl \longrightarrow B(SCH_3)_3 + 3\ (CH_3)_2NH{\cdot}HCl$$

Methyl thioborate was also prepared in 34% yield by the related reaction of boron trichloride with methyl mercaptan in the presence of trimethylamine as shown. The mercaptan was added to boron trichloride at −30° to give an intermediate complex which was converted to the indicated products by the addition of trimethylamine at 0°. The comparable reaction of boron tribromide with *n*-amyl mercaptan in the presence of pyridine led to *n*-amyl thioborate.

$$BCl_3 + 3\ CH_3SH + 3\ (CH_3)_3N \longrightarrow B(SCH_3)_3 + 3\ (CH_3)_3N{\cdot}HCl$$

A more convenient preparation of *n*-amyl thioborate was developed in which boron trichloride was added directly to a solution of *n*-amyl mercaptan in decane at 20°. The solution was refluxed at 100–180° and the solvent removed to give *n*-amyl thioborate in 57% yield. A comparable reaction of *n*-amyl mercaptan with boron tribromide did not give the expected thioborate. The successful preparation of *n*-amyl thioborate directly from the mercaptan and boron trichloride is interesting because it has been reported[1] that methyl thioborate could not be obtained from methyl mercaptan and either boron trichloride or boron tribromide.

EXPERIMENTAL[4]

Methyl thioborate. (a) *From tris(dimethylamino)borane.* A solution of 0.130 mole of hydrogen chloride in 50 ml. of diethyl ether was added to 7.16 g. (0.149 mole) of methyl

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[1] J. Goubeau and H. W. Wittmeier, *Z. anorg. u. allgem. Chem.*, **270**, 16 (1952).

[2] A. B. Burg and R. I. Wagner, *J. Am. Chem. Soc.*, **76**, 3307 (1954).

[3] M. F. Hawthorne, *J. Am. Chem. Soc.*, **82**, 748 (1960).

[4] Microanalyses were performed by Elek Microanalytical Laboratories. All experiments were carried out in an atmosphere of dry oxygen-free nitrogen.