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.

mercaptan and 6.20 g. (0.0434 mole) of tris(dimethylamino)-borane in 15 ml. of diethyl ether at −40°. The resulting reaction mixture was agitated for 0.74 hr. at 0° and 1.5 hr. at 25°. Insoluble dimethylamine hydrochloride was removed by filtration, and the filtrate fractionally distilled to give 3.52 g. (51.8% yield) of methyl thioborate, b.p. 102–103°/18 mm., n_D^{24} 1.5755. Burg[2] reported b.p. 100.1°/17.7 mm., and Goubeau[1] n_D^{20} 1.5788.

Anal. Calcd. for $C_3H_9S_3B$: B, 7.11. Found: B, 7.11.

It was found that explosive reactions resulted when thioborates were mixed with sodium peroxide, so standard peroxide fusion methods for boron should not be used with these compounds. However, boron can be determined in thioborates by sodium carbonate fusion, or by direct hydrolysis after initial removal of free mercaptan by boiling an acidified aqueous solution.

(b) *From boron trichloride.* A solid addition complex formed when methyl mercaptan (20.9 g., 0.4345 mole) was added to 15.4 g. (0.1315 mole) of boron trichloride in 100 ml. of pentane at −30°. The solid melted at −20° to give two immiscible liquids. Liquid trimethylamine (25.6 g., 0.434 mole) was added at 0° and the mixture stirred for 2 hr. at 0°. Insoluble trimethylamine hydrochloride was removed by filtration after standing overnight at room temperature. Distillation of the filtrate yielded pentane and 6.84 g. (34.2% yield) of a distillate fraction which was shown to be methyl thioborate.

n-Amyl thioborate from boron trichloride. Boron trichloride (4.52 g., 0.0386 mole) was added to a solution of 15.0 g. (0.144 mole) of *n*-amyl mercaptan in 25 ml. of decane at −20°. The solution was refluxed at 165–180° and the resulting hydrogen chloride trapped in aqueous sodium hydroxide. Fractional distillation of the reaction mixture gave 7.03 g. (56.8% yield) of *n*-amyl thioborate, b.p. 168–173°/0.2 mm., n_D^{24} 1.5145.

Anal. Calcd. for $C_{15}H_{33}S_3B$: C, 56.23; H, 10.38; B, 3.38; S, 30.02; mol. wt., 320. Found: C, 55.30; H, 10.00; B, 3.46; S, 29.17; mol. wt., 313 (cryoscopic in benzene).

In a comparable reaction, *n*-amyl thioborate was obtained in 27% yield when pyridine was added to a solution of boron tribromide and *n*-amyl mercaptan in decane.

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4-Hydroxyphenyltriphenylsilane and Its Glycidyl Ether

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Two organosilanes containing epoxy and phenyl groups have recently been described, namely, 4-epoxyethylphenyltrimethylsilane (4-trimethylsilylstyrene oxide)[1] and 4-(2,3-epoxypropoxy)phenyltrimethylsilane.[2] No other silanes of this type appear to be known. This report describes the first epoxy compound derived from tetraphenylsilane, namely, 4-(2,3-epoxypropoxy)phenyltriphenylsilane, III. In addition, an improved procedure is presented for the synthesis of 4-hydroxyphenyltriphenylsilane, I, and its sodium salt, II, from 4-bromophenol. An alternative preparation of II is also described, using 4-bromophenoxytrimethylsilane.

Although Benkeser and co-workers[3,4] have described a preparation of I wherein butyllithium and 4-bromophenol are treated in ether solution to give lithium 4-lithiophenoxide which is then treated with triphenylchlorosilane, repeated attempts to prepare I using this procedure have resulted in extremely poor yields. In this laboratory, it has been found that the yields of I are critically dependent upon whether butyllithium is added to 4-bromophenol or *vice versa*, a fact not mentioned in ref. 3. All experiments in which 4-bromophenol was added to butyllithium gave low yields, generally 10% or less of theoretical, whereas addition of butyllithium to the bromophenol produced yields of the *crude* sodium salt in excess of 80%. Although the yields were good in this procedure, it was evident that the phenoxide was heavily contaminated with by-products. As many as five recrystallizations from ethyl alcohol were necessary before specimens of II of constant melting point could be obtained. Naturally, during these recrystallizations, yields were reduced, so that it appeared expedient to search for an alternative and less time-consuming procedure which would give II in higher purity.

A synthesis of II was developed in which butyllithium was treated with 4-bromophenoxytrimethylsilane.[5] This blocking procedure reduced the number of by-products which were capable of forming when the unsubstituted bromophenol was employed. Reaction of the resulting 4-lithiophenoxytrimethylsilane with triphenylchlorosilane gave 4-triphenylsilylphenoxytrimethylsilane which, upon acid hydrolysis and extraction with sodium hydroxide, gave II in 50–60% yield. Two recrystallizations from ethyl alcohol were sufficient to give a product of constant melting point.

Although not required for the preparation of the glycidyl ether, the free phenol, I, was obtained from II by reaction in alcoholic solution with hydrochloric acid.

The glycidyl ether, namely, 4-(2,3-epoxypropoxy)phenyltriphenylsilane, III, was obtained by reacting II with excess epichlorohydrin and a small quantity of dilute sodium hydroxide solution at room temperature. This new epoxy derivative of tetraphenylsilane was synthesized by the sequence of reactions outlined on page 3032.

EXPERIMENTAL

Sodium 4-triphenylsilylphenoxide (II). *Method 1.* This compound was prepared using a modification of the procedure of Benkeser and co-workers.[3]

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(1) A. E. Senear, J. Wirth, and R. G. Neville, *J. Org. Chem.*, **25**, 807 (1960).

(2) R. G. Neville, *J. Org. Chem.*, **25**, 1063 (1960).

(3) R. A. Benkeser, C. E. DeBoer, R. E. Robinson, and D. M. Suave, *J. Am. Chem. Soc.*, **78**, 682 (1956); and private communication with Dr. Benkeser.

(4) C. Eaborn, *Organosilicon Compounds*, Butterworths, London, 1960, p. 421.

(5) This synthesis is a modification of that reported by J. L. Speier, *J. Am. Chem. Soc.*, **74**, 1003 (1952); and U. S. Pat. **2,611,777** (1952); **2,645,630** (1953).