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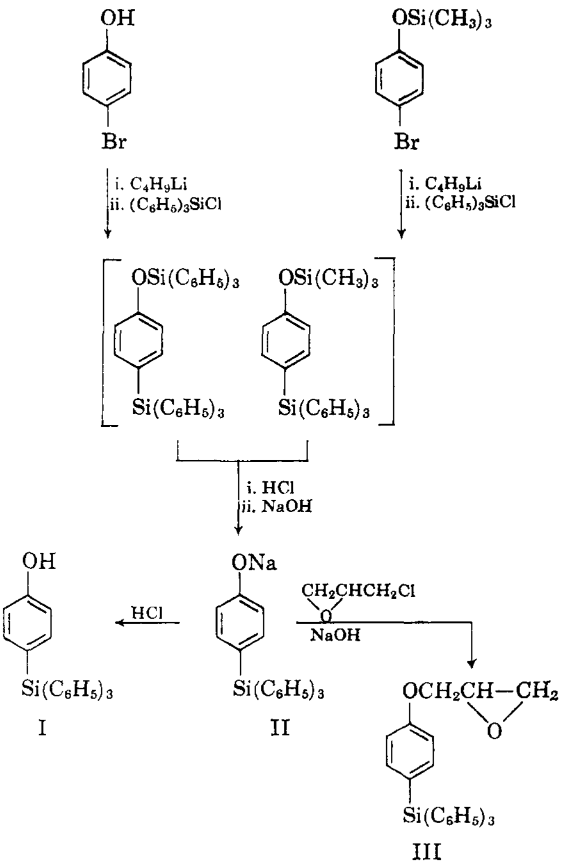
(1) A. E. Senear, J. Wirth, and R. G. Neville, *J. Org. Chem.*, **25**, 807 (1960).

(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).



A solution of 4-bromophenol (43.25 g.; 0.25 mole) in sodium-dried diethyl ether (100 ml.) was placed in a 1-l. three-necked flask fitted with reflux condenser, thermometer, motor-driven stirrer, dry nitrogen inlet and outlet tubes, and dropping funnel. The solution was cooled to −10°, and the system was swept out with dry nitrogen. Butyllithium, prepared in the standard manner[6] from *n*-butyl bromide (68.5 g.; 0.5 mole) and lithium ribbon (7.0 g.; 1.0 g.-atom) in ether (300 ml.), was added over a 0.5-hr. period at −10° to −20°. The mixture was stirred a further 0.5 hr. at −10° to +10°, then refluxed for 1.5 hr. A solution of triphenylchlorosilane (42.5 g.; 0.144 mole) in dry benzene (200 ml.)[7] was added over a 5-min. period to the hot solution, and the mixture refluxed for 24 hr. After cooling to room temperature, dilute hydrochloric acid (400 ml.)[8] was added. The temperature rose to 35°, and stirring was continued for 5 min. The organic layer was separated, shaken twice with 10% sodium hydroxide solution (100-ml. aliquots), then dried with anhydrous sodium sulfate followed by anhydrous magnesium sulfate. The pale yellow solution (approximately 350 ml.) was concentrated to about 50 ml. using a rotary evaporator heated by hot water. On cooling, the liquid began to crystallize. Addition of petroleum ether (b.p. 60–70°) (100 ml.), and stirring, gave a flocculent precipitate of white crystals. After filtering, washing with petroleum ether (100 ml.), and drying in a vacuum desiccator, 45 g. (88.9%) of sodium 4-triphenylsilylphenoxide was obtained. The glycidyl ether was prepared using this unpurified sodium salt.

After recrystallizing three to five times from 95% ethyl alcohol, pearly white crystals of the pure sodium salt were obtained, m.p. 185°.[9]

Anal. Calcd. for $C_{24}H_{19}ONaSi$: C, 77.00; H, 5.12. Found: C, 77.01; H, 4.91.

Sodium 4-triphenylsilylphenoxide (II). *Method 2.* In the same apparatus as was previously described, butyllithium (0.5 mole) in dry ether (100 ml.) was added to 4-bromophenoxytrimethylsilane[4] (122.5 g.; 0.5 mole) in ether (100 ml.) cooled to −20°. The mixture was refluxed for 7 hr., then cooled. Triphenylchlorosilane (147.25 g.; 0.5 mole) in dry tetrahydrofuran (250 ml., hydroquinone free) was added, and the mixture stirred and refluxed for 6 hr. Precipitated lithium salts were filtered off, and the yellow filtrate washed twice with water (300-ml. aliquots). To ensure that the intermediate 4-triphenylsilylphenoxytrimethylsilane had been completely hydrolyzed to the free phenol, the organic layer was shaken once with dilute hydrochloric acid (400 ml.)[8], then twice with 5% sodium hydroxide solution (250-ml. aliquots). After drying over anhydrous sodium sulfate, and evaporating off most of the solvent, petroleum ether (25 ml.) was added which precipitated the sodium salt of the silylphenol. The white crystals were filtered, washed with fresh petroleum ether, drained, and dried to yield 100.0 g. (53.5%) of II, a small quantity of which was twice recrystallized from ethyl alcohol to give a pearly crystalline solid of m.p. 185°. The infrared spectrum showed aromatic C═C at 1506 and 1590; Si—C_6H_5 at 1120 and 1430; and *p*-substitution at 825 cm.$^{-1}$

4-Triphenylsilylphenol (I). For purposes of characterization, this compound was prepared by dissolving the sodium salt (1.0 g.) in boiling 95% ethyl alcohol (25 ml.) and adding concentrated hydrochloric acid dropwise until slightly acid. A flocculent microcrystalline precipitate separated from the boiling solution. After cooling, the solid was filtered and recrystallized twice from alcohol giving 0.5 g. of 4-triphenylsilylphenol, m.p. 230–231°, in excellent agreement with the literature value.[3] The infrared spectrum showed prominent bands for Si—C_6H_5 at 1120 and 1429; *p*-substitution at 820; and phenolic OH at 3600 cm.$^{-1}$

4-(2,3-Epoxypropoxy)phenyltriphenylsilane (III). Epichlorohydrin (45.75 g.; 38.1 ml.; 0.5 mole) and II (37.4 g.; 0.1 mole) were placed in a 250 ml. Erlenmeyer flask. On heating the mixture to about 70°, and shaking, the phenoxide dissolved. The mixture was then cooled to 20°, sodium hydroxide (2.0 g.; 0.05 mole) in water (20 ml.) was added, and the flask securely stoppered. After shaking mechanically for 24 hr. at room temperature, the mixture was filtered, and the filtrate extracted with ether (100 ml.). The extract was washed with water (100 ml.) and dried over anhydrous sodium sulfate. On evaporating the ether, 21.0 g. (51.5%) of white crystalline solid separated. Two recrystallizations from benzene, using charcoal, yielded colorless stubby crystals of III, m.p. 152°.

Anal. Calcd. for $C_{27}H_{24}O_2Si$: C, 79.4; H, 5.88. Found: C, 79.77; H, 5.64.

The infrared spectrum showed bands due to Si-C_6H_5 at 1125 and 1430, and strong bands due to the oxirane ring at 865, 1165, and 1265 cm.$^{-1}$

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(6) A. I. Vogel, *A Text-Book of Practical Organic Chemistry*, Longmans, Green and Co., London, 1956, p. 932.

(7) Filtered from insoluble material always present in commercially supplied "95%" triphenylchlorosilane.

(8) Prepared by mixing 100 ml. of concd. hydrochloric acid with 300 ml. of water.

(9) Melting points are uncorrected.