Structural Studies. Isomaltulose was hydrolyzed by heating for 1 hr. in 0.25*N* hydrochloric acid. Paper chromatography showed approximately equal amounts of glucose and fructose.

Isomaltulose (68 mg.) was converted to 63 mg. of the phenylosazone, which, when crystallized from wet ethyl acetate, melted at 203–204° (cor.). The phenylosazone of isomaltose was found to melt at 201–202° (cor.). Both osazones were cleaved with sodium periodate to yield the crystalline 1,2-bisphenylhydrazone of mesoxalaldehyde. Oxidation of the phenylosazone of isomaltulose with copper sulfate gave 23 mg. of a phenylosotriazole [m.p. 179–180° (cor.)], shown by mixed melting-point test and x-ray diffraction patterns to be identical with the phenylosotriazole prepared from pure isomaltose.

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Synthesis of 4-(2,3-Epoxypropoxy)phenyltrimethylsilane

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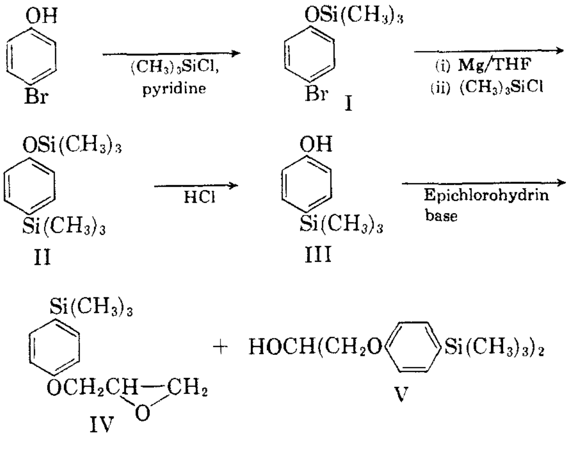
Organosilicon compounds containing epoxide groups are of quite recent origin. Martin[1] reported the preparation of glycidyl silicon ethers by reaction of glycidol with chlorosilanes in the presence of a hydrogen chloride acceptor (*e.g.*, triethylamine). About the same time, Andrianov and Dubrovina[2] reported the synthesis of alkylacetoxyepoxysilanes; and Brynolf[3] prepared 3,4-epoxybutyltrimethylsilane by the reaction of trimethylsilylmethylmagnesium bromide with epichlorohydrin followed by treatment with base. Very recently, Plueddemann and Fanger[4] reported an interesting series of epoxyorganosiloxanes formed either by peracetic acid epoxidation of olefinic organosilicon compounds, or by addition of silicon hydrides across the olefinic bond of unsaturated epoxy compounds.

Evidently silicon analogs of commercial epoxy (Epon) resins have not been described. In this paper we wish to report the synthesis of 4-(2,3-epoxypropoxy)phenyltrimethylsilane, IV, a silicon analog of the well known phenyl glycidyl ether.[5,6]

This new type of epoxysilane was synthesized using the following sequence of reactions:



Compounds I, II, and III have been reported previously,[7-10] although modifications of the published procedures were employed in the present work. Reaction of 4-trimethylsilylphenol (III) with epichlorohydrin in basic solution at room temperature (20°) was found to proceed readily, the optimum yield of IV being obtained at about a 1:3 molar ratio of III with epichlorohydrin. The use of less epichlorohydrin resulted in the formation of larger amounts of the secondary product, 1,3-bis(4-trimethylsilylphenoxy)-2-propanol, V, by reaction of IV with III.

EXPERIMENTAL

4-Bromophenoxytrimethylsilane. I. A mixture of 4-bromophenol (865 g., 5.0 moles), anhydrous benzene (900 ml.), and pyridine (395 g., 5.0 moles) was cooled in an ice bath at 0–5°; then trimethylchlorosilane (542.5 g., 5.0 moles) in benzene (500 ml.) was added dropwise with stirring. Throughout the addition care was taken to maintain the temperature in the range 5–20°. After stirring for 3 hr., and standing overnight, the precipitated pyridinium chloride was filtered. The filtrate was distilled at atmospheric pressure to remove most of the benzene, and the residue was distilled *in vacuo*, the fraction of b.p. 120–130°/20–30 mm. being collected. Refractionation gave pure I of b.p. 122°/20 mm., in good agreement with the literature value.[7,9] The yield was 882 g. (72%).

It should be noted that specimens of this compound partially decomposed to 4-bromophenol on standing for several weeks in tightly-stoppered Pyrex glass bottles. The infrared spectrum of freshly prepared I showed no bands due to hydroxyl. These developed gradually and it was considered inadvisable to use specimens of I older than about 1 month for Grignard syntheses.

4-Trimethylsilylphenoxytrimethylsilane. II. A modification of the synthesis of Frisch and Shroff[9] was employed using tetrahydrofuran rather than ether as solvent. This was

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[1] R. W. Martin, U. S. Patent **2,730,532** (1956).

[2] K. A. Andrianov and V. G. Dubrovina, *Doklady Akad. Nauk S.S.S.R.*, **108,** 83 (1956).

[3] S. Brynolf, *Acta Chem. Scand.*, **10** (5), 883 (1956).

[4] E. P. Plueddemann and G. Fanger, *J. Am. Chem. Soc.*, **81,** 2632 (1959).

[5] T. Lindeman, *Ber.*, **24,** 2145 (1891).

[6] D. R. Boyd and E. R. Marle, *J. Chem. Soc.*, 838 (1908).

[7] J. L. Speier, *J. Am. Chem. Soc.*, **74,** 1003 (1952).

[8] J. L. Speier, U. S. Patents **2,611,776, 2,611,777** (1952); **2,645,630** (1953).

[9] K. C. Frisch and P. D. Shroff, *J. Am. Chem. Soc.*, **75,** 1249 (1953).

[10] K. C. Frisch, U. S. Patent **2,711,417** (1955).

significant in view of the fact that the time for Grignard formation was 2 hr. instead of 18 hr. with ether.

In a 5-l. three-necked flask, fitted with motor-driven stirrer, thermometer, and dropping funnel, were placed the following reactants: magnesium turnings (27 g., 1.1 g.-atoms), sodium-dried tetrahydrofuran (tetrahydrofuran, distilled free from hydroquinone, 50 ml.), and methyl iodide (5 ml.). The mixture was gently warmed on the water bath until methylmagnesium iodide had formed. Tetrahydrofuran (150 ml.) was added and the mixture heated to gentle reflux. 4-Bromophenoxytrimethylsilane (245 g., 1.0 mole) in tetrahydrofuran (400 ml.) was added dropwise with vigorous stirring over a 1-hr. period, after which the mixture was refluxed a further hour then cooled to 10°. Trimethylchlorosilane (120 g., 1.1 moles) was added with stirring, the mixture was then brought to reflux for 1 hr., and allowed to cool overnight. The crystallized magnesium salts were dissolved in water (500 ml.), the tetrahydrofuran layer separated, washed four times with water, dried over anhydrous sodium sulfate, and distilled. The colorless liquid fraction of b.p. 132–135°/22–44 mm. was collected in 184 g. (77.4%) yield. Refractionation yielded a liquid of b.p. 132–133°/25 mm., in agreement with the literature[7] value.

4-Trimethylsilylphenol. III. 4-Trimethylsilylphenoxytrimethylsilane (48.0 g., 0.2 mole) in 95% ethyl alcohol (15 ml.) was acidified with *one* drop of concd. hydrochloric acid then diluted with water (6 ml.). After shaking for 5 min., the mixture was diluted to turbidity with more water and then allowed to stand for 15 min. The lower aqueous layer was discarded and the organic layer was washed twice with 50-ml. aliquots of water. The organic layer was transferred to a large dish and the alcohol allowed to evaporate in the air. 4-Trimethylsilylphenol rapidly crystallized in theoretical yield, m.p. 74°, in agreement with the published values.[7,9]

As difficulty was initially encountered in the preparation of this compound it is important to emphasize the following precautions to be taken in its synthesis. Only 1 very small drop of concd. acid is required to cleave the trimethylsiloxy group to the phenol, and the temperature must be kept below 25°. The use of more acid, or heating, results in some cleavage of the 4-trimethylsilyl group to phenol itself. The preparation of Frisch and Shroff,[9] in which II is refluxed in dilute ethanolic acid, could not be reproduced in this laboratory. The atmosphere of the laboratory was found to be sufficiently acidic to cause some cleavage of III to phenol when specimens were exposed in open dishes for about 1 week. The silylphenol could be stored in tightly capped bottles, or as the sodium salt.

4-(2,3-Epoxypropoxy)phenyltrimethylsilane. IV. 4-Trimethylsilylphenol (166 g., 1.0 mole) was dissolved in a solution of sodium hydroxide (50 g., 1.25 moles) in water (500 ml.) and isopropyl alcohol (50 ml.). Epichlorohydrin (277 g., 3.0 moles) was then added, the whole stoppered and shaken vigorously for 15 min. and allowed to stand at room temperature for 20 hr. A pale yellow organic layer floating on a dark brown aqueous phase resulted. The mixture was extracted with ether, washed twice with water, dried over anhydrous potassium carbonate, and distilled to remove most of the ether. The residue was distilled *in vacuo* and the fraction of b.p. 145–185°/20 mm. was collected as a colorless liquid in 152 g. (68.5%) yield. The main fraction distilled at 170–172°/20 mm. Redistillation gave 117 g. of colorless oil, b.p. 170°/20 mm.

Anal. Calcd. for $C_{12}H_{18}O_2Si$: C, 64.80; H, 8.16. Found: C, 64.84; H, 8.11.

1,3-Bis(4-trimethylsilylphenoxy)-2-propanol. V. The residue remaining after distillation of IV was recrystallized from isopropyl alcohol and a white crystalline solid, m.p. 74°, was obtained. The infrared spectrum showed strong absorption in the hydroxyl region together with three strong bands due to the trimethylsilyl group at 1248, 838, and 759 cm.$^{-1}$ [11,12]

In the preparation of phenyl glycidyl ether[6] under similar conditions 1,3-diphenoxy-2-propanol is formed as a by-product. By analogy, this compound was concluded to be 1,3-bis(4-trimethylsilylphenoxy)-2-propanol.

Anal. Calcd. for $C_{21}H_{32}O_3Si_2$: C, 64.87; H, 8.31. Found: C, 64.70; H, 8.34.

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A New Synthesis of Organothiosilanes

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Compounds containing the silicon-sulfur linkage have been prepared by the reactions of silicon (IV) sulfide with alkyl silicates,[1] silylamines with hydrogen sulfide or thiphenols,[2,3] silyl iodide with mercury (II) sulfide,[4] silicon tetrachloride with hydrogen sulfide,[5] silicon tetrachloride with sodium hydrosulfide,[6] and $Pb(SR)_4$ types with silicon tetrachloride.[7a,b]

Solutions of triphenylsilyllithium[8] in tetrahydrofuran react smoothly with sulfur to give the lithium salt of triphenylsilanethiol (I):

$$(C_6H_5)_3SiLi + S \longrightarrow \underset{\text{I}}{(C_6H_5)_3SiSLi} \xrightarrow{RX} (C_6H_5)_3SiSR$$

$$R = -CH_3\ (\text{II}),\ -CH_2C_6H_5\ (\text{III}),\ -COC_6H_5\ (\text{IV})$$

Subsequent reaction of intermediate I with methyl iodide, benzyl chlorde, or benzoyl chloride gives rise to (methylthio)triphenylsilane (II), (benzylthio)triphenylsilane (III), and (benzoylthio)triphenylsilane(IV), respectively, in good yields. To our knowledge, the latter compound (IV), is the first reported to contain the Si—S—CO— linkage.

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