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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(Methylthio)triphenylsilane(II) is cleaved by phenyllithium to give tetraphenylsilane in a reaction analogous to the well-known cleavages of siloxanes by organometallic reagents.

$$(C_6H_5)_3SiSCH_3 + C_6H_5Li \longrightarrow (C_6H_5)_4Si + CH_3SLi$$

No observable reaction was noted between the lithium salt of triphenylsilanethiol (I) and iodobenzene, chlorotrimethylsilane, or chlorotriphenylsilane.

## EXPERIMENTAL[9]

*Preparation of the intermediate lithium salt of triphenylsilanethiol* (I). To a stirred suspension of 0.62 g. (0.0193 g.-atom) of sulfur in 25 ml. of tetrahydrofuran was added 50 ml. of a tetrahydrofuran solution of triphenylsilyllithium[8] prepared by the cleavage of 5.0 g. (0.00965 mole) of hexaphenyldisilane with excess lithium. During the addition, some heat was given off, and the solution became almost black in appearance. When the addition was complete, Color Test I[10] was negative, indicating that the triphenylsilyllithium had reacted completely.

Solutions of I prepared in this manner were used in the following three reactions.

*Reactions of intermediate I. A. With methyl iodide.* Excess methyl iodide was added to a solution of I prepared in the manner described. The dark color of the solution was discharged, and heat was evolved. The tetrahydrofuran was strip distilled. The resulting oil was fractionated to give 4.05 g. (76%) of crude (methylthio)triphenylsilane, b.p. 145–150° (0.06 mm.), which solidified on standing. Recrystallization from petroleum ether (b.p. 60–70°) gave 3.07 g. (52%) of pure product, m.p. 83–84°.

*Anal.* Calcd. for $C_{19}H_{18}SSi$: Si, 9.15. Found: Si, 9.33, 9.28.

*B. With benzyl chloride.* To a solution of I prepared in the manner described was added excess benzyl chloride. The dark color of the solution was discharged over a period of about 30 min. The tetrahydrofuran was stripped off. Distillation of the residual oil gave 3.33 g. (45%) of crude (benzylthio)triphenylsilane (III), b.p. 172–177° (0.015 mm.). Two recrystallizations from petroleum ether (b.p. 60–70°) gave 2.7 g. (36%) of crystals, m.p. 92–94°.

*Anal.* Calcd. for $C_{25}H_{22}SSi$: Si, 7.33. Found: Si, 7.08, 7.27.

*C. With benzoyl chloride.* Addition of 3.05 g. (0.0217 mole) of benzoyl chloride to a solution of I, prepared in the manner described, resulted in a fast exothermic reaction. The tetrahydrofuran was stripped off the almost clear solution. The resulting oil was distilled to give 4.48 g. (59%) of crude (benzoylthio)triphenylsilane (IV), b.p. 183–189° (0.01 mm.). Recrystallization from anhydrous petroleum ether (b.p. 60–70°) gave 2.75 g. (36%) of yellow needles, m.p. 128–129°. The infrared spectrum of the product showed a normal carbonyl absorption peak at 5.9 $\mu$.

*Anal.* Calcd. for $C_{25}H_{20}OSSi$: Si, 7.08. Found: Si, 7.10, 6.87.

*Cleavage of (methylthio)triphenylsilane* (II) *by phenyllithium.* To a stirred solution of 2.0 g. (0.00653 mole) of II in 20 ml. of ether was added 32 ml. of an ethereal solution containing 0.00978 mole of phenyllithium. The reaction mixture was hydrolyzed with water and filtered to give 1.97 g. (89%) of tetraphenylsilane, m.p. 233–235°, identified by a mixed melting point with an authentic specimen. The filtrate smelled strongly of a sulfur compound, presumably methyl mercaptan.

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# Consecutive Rate Constants for Saponification of the Isomeric Diethyl Phthalates

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In our recent publication[2] the saponification and acid-catalyzed hydrolysis of the diethyl phthalates and methoxyphthalates were reported. The rates of saponification of the individual ester groups in diethyl 2- and 5-methoxyisophthalates were calculated by the method of Frost and Schwemer.[3] Unfortunately, the tables in the Frost and Schwemer publication did not include time ratios for values of $k_1/k_2$ greater than 10.0, where $k_1$ and $k_2$ are, respectively, the rate constants for the consecutive saponification of first one and then the remaining carbethoxyl group of the diester molecule. This made it necessary to obtain by tedious calculation and interpolation the value of $k_1/k_2$ for diethyl 5-methoxyisophthalate which is greater than 10.0.

A computer program has been written[4] to extend broadly the tables of Frost and Schwemer, and thereby greatly facilitate the calculation of the consecutive or separate rate constants from a much wider range of experimental data. By using the new extended tables obtained from the computer program together with our previous experimental results,[2] it has been possible to calculate $k_1$ and $k_2$ for the saponification of the diethyl esters of the isomeric phthalic acids, and to recalculate those for 2- and 5-methoxyisophthalic acids. The recalculation of $k_1$ and $k_2$ for the latter two methoxy compounds has revealed that the constants initially reported[2] are one-half the true values.

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