hexaphenylcyclotrisiloxane (hereafter called trimer) from diphenyldichlorosilane (DPDS).

It has now been found that the trimer can be obtained readily by the reaction of DPDS with zinc oxide: When one mol. of DPDS was added to one and one half to two mol. of zinc oxide in inert solvents, reaction occurred exothermally. Trimer was obtained from the reaction product in a yield of 96 % (mean). Zinc chloride was determined as zinc hydroxide by neutralization with aqueous base.

Stoichiometry supports the following equation:

$$ZnO + (C_6H_5)_2SiCl_2 \longrightarrow ZnCl_2 + 1/3[(C_6H_5)_2SiO]_3$$

Other anhydrous reagents[2] (cupric oxide, lead oxide, silver oxide, manganese dioxide, cupric sulfate, ferric sulfate, zinc sulfate, nickel sulfate, ferric oxalate, cupric carbonate basic, etc.) were found to react with DPDS in substantially similar manner.

EXPERIMENTAL

Reagents. Purified-grade diphenyldichlorosilane was received from the Shin-etsu Chemical Industrial Co. Reagent-grade zinc oxide was finely powdered after prolonged drying. Methyl acetate was purified according to the ordinary method.

Procedure. A typical procedure is as follows: When a solution of diphenyldichlorosilane in methyl acetate (50 g., 0.2 mol., of DPDS, dissolved in 100 ml. of methyl acetate) was added portion-wise to a shaking flask which contained 24 g., 0.3 mole, of zinc oxide and 200 ml. of methyl acetate, an exothermic reaction occurred gradually. After the addition of DPDS was complete, the reaction mixture was gently refluxed for about 10 min., the color change of crystal violet[3] was used to determine completion of the reaction.

Benzene (200 ml.) was added to the reaction mixture to dissolve the silicon-containing product, and the resulting mixture, cooled to room temperature, was filtered by suction. The filtrate was shaken with about 400 ml. of distilled water to remove zinc chloride.

The top layer was separated, ethanol (200 ml.) was added to it, and the solution was evaporated to dryness on a water bath. A white crystalline mass melting at 177–180° and mixed with a small amount of oily liquid, was obtained. Further purification was effected by recrystallization from ethyl acetate, whereby 38 g. (97%) of pure trimer melting at 188–189° was obtained as elongated hexagonal plates.

Anal. Calcd. for $C_{36}H_{30}Si_3O_3$: Si, 14.16; OH/mol., 0.00; mol. wt., 594. Found: Si, 14.8; OH/mol., 0.0 (Karl Fischer titration[4]); mol. wt., 580–600 (Rast).

The x-ray powder pattern of the trimer obtained showed the major part to be orthorhombic trimer[5] and a minor amount to be triclinic trimer.[5]

From the bottom layer, 19 g. (96%) of zinc hydroxide was obtained by aqueous treatment with ammonium hydroxide using phenolphthalein as an indicator.

Although some other oxides and sulfates were also found to produce trimer and chlorides, respectively, most effective results (highest yield of trimer, greatest simplicity in procedure) were achieved by using zinc oxide as a reactant, whereby the marked dehydrating effect of the chloride resulted in almost a quantitative formation of the trimer.

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Synthesis of Tetra(perfluoroalkoxy)silanes

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The first reported synthesis of a tetraalkoxysilane was made by von Ebelman.[1] Since that time many tetraalkoxysilanes have been reported in literature.[2,3,4,5] Reaction 1 is most generally used for the preparation of these compounds:[6,7]

$$4SiCl_4 + 10\ ROH \longrightarrow ROSiCl_3 + (RO)_2SiCl_2 + (RO)_3SiCl + (RO)_4Si + 10HCl \quad (1)$$

A modification of the method of Helferich and Hausen[8] was employed to make a number of previously unreported tetra(perfluoroalkoxy)silanes. The method consisted of reacting tetrachlorosilane and a 10% molar excess of perfluorinated alcohols in an anhydrous medium at −10°. Hydrogen chloride produced during the reaction was removed by refluxing and by purging the reaction mixture with dry inert gas. The desired silanes were recovered by vacuum distillation.

Molar excesses of alcohol were used, not only to promote the formation of the tetra-substituted silanes, but also to prevent any reaction between silicon tetrachloride and the tetra-substituted silanes during refluxing or distillation.[9]

$$SiCl_4 + Si(OR)_4 \longrightarrow 2Cl_2Si(OR)_2 \quad (2)$$

Before distillation, the crude mixture of silanes was percolated through a column of activated, dry silica gel to remove the acidic materials which

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TABLE I

PROPERTIES OF TETRA(PERFLUOROALKOXY)SILANES

R	B.P./Mm. Hg	$(RO)_4Si$ F.P.[a]	d_4^{20a} and	$d_4^{71.1}$	n_D^{20}	Viscosity, cp.[a] 20.0 and	71.1
$CF_3—CH_2—$[b]	155.5–157/$_{743}$	−25	1.5107	1.4089	1.30206	2.2089	1.240
$HCF_2CF_2CH_2—$	117–118/$_4$	<−68	1.5927	1.5100	1.33174	18.92	3.583
$CF_3(CF_2)_2CH_2—$	96–97/$_4$	<−68	—	1.5740	1.30088	7.613	1.931
$H(CF_2—CF_2)_2CH_2—$	156–159/$_{2.5}$	<−68	1.8150	1.6440	1.32622	42.75	5.820
$H(CF_2—CF_2)_3CH_2—$	201–204/$_3$	<−68	—	1.7181	—	108.8	12.23
$H(CF_2—CF_2)_4CH_2—$	235–240/$_{2.5}$[c]	—	—	—	—	—	—

[a] Freezing points, densities, and viscosities were determined by T. M. Verdura. [b] Pennsalt Chemicals Corp. Booklet DC-1254, *Trifluoroethanol*, b.p. 60–61/25 mm. [c] Material decomposed during distillation.

are deleterious to hydrolytic stability. The mechanism that has been postulated[10] for this hydrolyzation is as follows:

$$\gt SiOR + H_2O \longrightarrow ROH + \gt SiOH \longrightarrow {}^1/_2 \gt SiOSi \lt + {}^1/_2H_2O \quad (3)$$

The corresponding alcohol and polymeric siloxanes are produced, leading to the precipitation of insoluble polymers or, ultimately, of silica.

All the compounds listed in Table I, except tetra (1,1-dihydrotrifluoroethoxy)silane, are new compounds.

EXPERIMENTAL[11]

Starting materials. Tetrahydrofuran (Eastman Kodak Co., white label) was refluxed over calcium hydride until no more bubbles evolved upon further calcium hydride addition. The tetrahydrofuran was then distilled from the calcium hydride through a ½ by 12 inch Vigreux column, and the portion distilling at 64–64.5° collected. Water content was less than 0.003% by test with Karl Fischer reagent.[12] *Tetrachlorosilane* (Tech. Grade) was purified by distillation. *1,1-Dihydrotrifluoroethanol* (Pennsalt Chemicals Corp.) was distilled from anhydrous calcium sulfate (Drierite), and the portion distilling at 72–72.5° collected. *1,1-Dihydroheptafluorobutanol* (Minnesota Mining & Mfg. Co.) was distilled, and the portion distilling at 74–74.6° collected. The *trihydroperfluoroalcohols*[13] (du Pont) were used as received. The inert gases used for purging of the reaction mixtures were dried by passage through Linde molecular sieve, Type 4A.

Apparatus. The all-glass apparatus used in the preparations and distillations was protected from atmospheric moisture by Drierite-filled tubes.

Tetra (1,1-dihydrotrifluoroethoxy)silane. While 220.1 g. (2.2 mol.) of 1,1-dihydrotrifluoroethanol was rapidly stirred, 84.9 g. (0.50 mol.) of tetrachlorosilane was added over a period of 1 hr. After the addition was completed, the solution was refluxed for 2 hr., while hydrogen chloride was evolved at a decreasing rate. The reaction mixture was cooled to 25° and percolated through an anhydrous silica gel column, using dry tetrahydrofuran as eluant. The product was then distilled through a ½ by 12 inch Vigreux column, and the clear fraction boiling at 155.5–157° (743 mm.) was collected.

Tetra (1,1,3-trihydrotetrafluoropropoxy)silane. The preparation of this compound will illustrate the method used for the preparation of the remaining compounds listed in Table I. A solution of 290.5 g. (2.2 mol.) of 1,1,3-trihydrotetrafluoropropanol in an equal volume of tetrahydrofuran was cooled to −14°. While this solution was vigorously stirred, a solution of 84.9 g. (0.5 mol.) of tetrachlorosilane in an equal volume of tetrahydrofuran was added over a 1-hr. period. During the addition the solution temperature was maintained below −10°. The solution was then refluxed for 2 hr. with the generation of copious amounts of hydrogen chloride. The heat source was removed and the solution purged with a dry inert gas for 2 hr. Tetrahydrofuran and excess alcohol were removed under vacuum at room temperature, and the residue vacuum distilled through a ½ by 12 inch Vigreux column. The clear colorless fluid distilling at 117–118° (4 mm.) was collected.

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(13) The author wishes to thank A. C. Haven of du Pont who supplied samples of alcohols.