[CONTRIBUTION FROM THE INSTITUTE OF POLYTECHNICS, OSAKA CITY UNIVERSITY]

Synthesis of Some Methyldisilanes Containing Functional Groups

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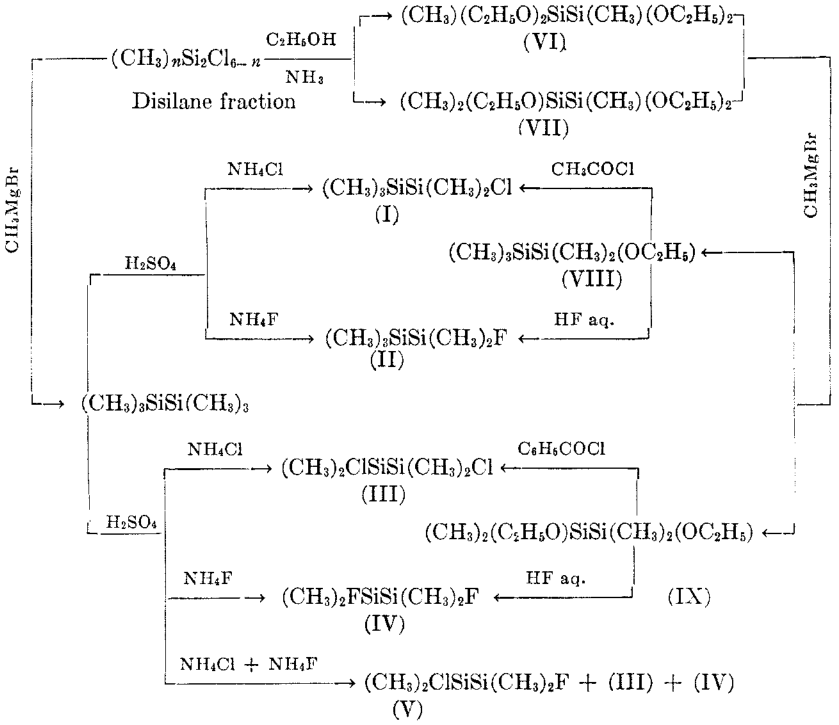
Received May 23, 1956

Nine methyldisilanes which contain functional groups such as chlorine, fluorine, or ethoxyl, linked to silicon have been prepared starting from the higher-boiling residue produced in the direct synthesis of methylchlorosilanes. Demethylation of hexamethyldisilane by concentrated sulfuric acid was found to take place in the analogous way to that of 1,4-bis(trimethylsilyl)butane in the literature,[1] but our reaction proceeded in two distinct stages: first, a heterogeneous but a fast step and second, a homogeneous but a slow one. The first step corresponded to cleavage of one methyl from one silicon, while the second involved cleavage of the second methyl from another silicon. Treatment of the resulting sulfuric acid solution with ammonium chloride or fluoride, or a mixture of both halides proved to be a most satisfactory method for the synthesis of compounds of the general formulas, $(CH_3)_3SiSi(CH_3)_2X$ and $(CH_3)_2XSiSi(CH_3)_2X$, with X = Cl and F. Hydrolysis of the difunctional disilanes resulted in the formation of the cyclic dimer, $[—(CH_3)_2SiSi(CH_3)_2O—]_2$.

Three methods are generally employed for the preparation of organosubstituted disilanes: alkylation of hexahalodisilanes using appropriate organometallic compounds [1a–5] alkali metal condensation of triorganosilanes or triorganohalosilanes;[6–11] or reactions with triphenylsilylpotassium.[12,13] None of these methods, however, is advantageously applied to the preparation of methyldisilanes containing reactive functional groups.

In previous work from this laboratory it was shown that the distillation residue from the direct synthesis of methylchlorosilanes is composed essentially of three types of compounds having the

REACTION CHART I



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(1) Sommer and Ansul, *J. Am. Chem. Soc.*, **77**, 2482 (1955).

(1a) Friedel and Ladenburg, *Ann.*, **203**, 251 (1880).

(2) Bygden, *Ber.*, **45**, 707 (1912).

(3) Martin, *Ber.*, **46**, 3294 (1913).

(4) Schumb and Saffer, *J. Am. Chem. Soc.*, **61**, 363 (1939); **63**, 93 (1941).

(5) Wilkins, *J. Chem. Soc.*, 3409 (1953).

(6) Schlenk, Penning, and Rackey, *Ber.*, **44**, 1178 (1911).

(7) Kipping, *J. Chem. Soc.*, **117**, 647 (1921).

(8) Kraus and Nelson, *J. Am. Chem. Soc.*, **56**, 195 (1934).

(9) Gilman and Dunn, *J. Am. Chem. Soc.*, **73**, 5077 (1951).

(10) Gilman, Wu, Hartzfeld, Guter, Smith, Goodman, and Eidt, *J. Am. Chem. Soc.*, **74**, 561 (1952).

(11) Gilman, Ingham, and Smith, *J. Org. Chem.*, **18**, 1743 (1953).

(12) Benkeser and Severson, *J. Am. Chem. Soc.*, **73**, 1424 (1951).

(13) Gilman and Wu, *J. Am. Chem. Soc.*, **73**, 4031 (1951); **75**, 3762 (1953).

frameworks: SiOSi, Si-Si, and $SiCH_2Si$.[14,15] As a part of a program of study aimed at the utilization of methylchlorosilane residue it was of primary interest to us to prepare mono- and di-functional methyldisilanes, since they would be of considerable interest from the standpoint not only of the synthetic chemistry but also of other various lines, including molecular structure studies. In this paper we report several disilanes having the general formulas, $(CH_3)_3SiSi(CH_3)_2X$ and $(CH_3)_2XSiSi(CH_3)_2X$, where X stands for Cl, F and OC_2H_5.

It was already reported[14] that the fraction boiling over the range about 150–160° (hereafter called the disilane fraction), from the methylchlorosilane residue, consists essentially of a mixture of methylchlorodisilanes; however, no time-consuming fractional distillation could be sufficient for the expedient isolation of any substance in pure state. It therefore seemed necessary to establish any advantageous method for the synthesis. For this purpose, two approaches proved to be particularly convenient. Reactions employed in the present work are summarized in Reaction Chart I.

Method I involved demethylation of hexamethyldisilane by concentrated sulfuric acid, followed by treatment of the resulting sulfuric acid solution with ammonium chloride or fluoride.

As previously reported,[13] hexamethyldisilane of high purity was easily prepared through the reaction of methylmagnesium bromide with the disilane fraction and treatment of methylmagnesium bromide with the disilane fraction and treatment of the product with cold sulfuric acid so as to completely eliminate possible contamination by hexamethyldisiloxane. The demethylation process by sulfuric acid is a modification of a reaction recently discovered and applied extensively to the syntheses of various types of organopolysiloxanes by L. H. Sommer and coworkers,[16–21] who noted that under proper conditions concentrated sulfuric acid was capable of cleaving only one methyl group from certain trimethylsilyl organic structures. This process was not only easily carried out, but also of much more interest in our case where two trimethylsilyl groups were directly linked to each other. When a heterogenous mixture of hexamethyldisilane and excess concentrated sulfuric acid was vigorously stirred at a temperature of 20–35°, first one molar equivalent of methane was evolved at a regular rate within a few hours. At this point the velocity of gas evolution suddenly diminished, although a homogeneous solution had resulted. It usually required more than 30 hours until the evolution of the second one molar equivalent of methane was completed. Treatment of the sulfuric acid solution with ammonium chloride (or fluoride) at the point either of the first or of the second end of methane evolution gave pentamethylchlorodisilane (I) [or pentamethylfluorodisilane (II)] or 1,1,2,2-tetramethyl-1,2-dichlorodisilane (III) [or 1,1,2,2-tetramethyl-1,2-difluorodisilane (IV)], respectively, in good yields. Addition to the sulfuric acid solution of a mixture of ammonium chloride and fluoride in an equimolar proportion led to the formation of 1,1,2,2-tetramethyl-1-chloro-2-fluorodisilane (V) as well as compounds III and IV. Further proof of structure for compounds III and IV was afforded by their conversion, on hydrolysis, to the cyclic dimer (X), as shown later.

It is to be noted that a small quantity of trimethylchlorosilane or trimethylfluorosilane also should be formed in the above reaction, indicating cleavage of Si–Si linkage to a small extent.

Method II comprised ethanolysis of the disilane fraction, followed by partial methylation with the Grignard reagent, and then chlorination with acyl chlorides at elevated temperatures, or fluorination with aqueous hydrogen fluoride at 0°.

Ethanolysis of the disilane fraction was generally carried out with slightly more than an equivalent quantity of absolute ethanol and any hydrogen chloride-acceptor, dry ammonia gas being used in most cases. Fractional distillation of the ethanolysis product[22] yielded mainly 1,2-dimethyl-1,1,2,2-tetraethoxydisilane (VI) and/or 1,1,2-trimethyl-1,2,2-triethoxydisilane (VII), depending upon the original disilane fraction used. The Si–Si linkage in these two compounds was found to be so susceptible to cleavage by basic reagents that their structure proof was obtained without difficulty.[23] Thus, compound VI was cleaved, on treatment with a slight excess of absolute ethanol containing catalytic amount of sodium ethoxide, to afford methyltriethoxysilane in 91% yield.

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(14) Kumada and Yamaguchi, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **57**, 175 (1954); *Chem. Abstr.*, **49**, 11542 (1955).

(15) Recently, several utilizations of the methylchlorosilane residue have been disclosed in the patent literature: (a) Mohler and Sellens, U. S. Patents 2,598,434 and 2,598,435, May 27, 1952 (To General Electric Co.); (b) Barry and Gilkey, U. S. Patent 2,681,355, June 15, 1954 (To Dow Corning Corp.); (c) Clark, British Patent 674,591, June 25, 1952 (To Dow Corning Corp.); and (d) Kumada and Kuriyakawa, Japanese Patents 211,226, Feb. 5, 1954 and 212,568, Mar. 30, 1954 (To Tokyo-Shibaura Elec. Co., Ltd.).

(16) Sommer, Marans, Goldberg, Rockett, and Pioch, *J. Am. Chem. Soc.*, **73**, 882 (1951).

(17) Sommer, Marans, Goldberg, Rockett, and Kerlin, *J. Am. Chem. Soc.*, **75**, 2932 (1953).

(18) Sommer, Barie, and Gould, *J. Am. Chem. Soc.*, **75**, 3765 (1953).

(19) Sommer, Goldberg, Barnes, and Strong, *J. Am. Chem. Soc.*, **76**, 1609 (1954).

(20) Sommer and Ansul, *J. Am. Chem. Soc.*, **77**, 2482 (1955).

(21) Sommer, English, Ansul, and Vinons, *J. Am. Chem. Soc.*, **77**, 2485 (1955).

(22) A relatively small amount of methyltriethoxysilane was always a by-product, thus indicating that a slight amount of silicon-silicon cleavage took place.

(23) In contrast to VI and VII, mono- and di-functional methyldisilanes, such as VIII and IX, were found very stable to cleavage by bases of moderate concentrations even under reflux.

$$\underset{\text{VI}}{(CH_3)(C_2H_5O)_2SiSi(CH_3)(OC_2H_5)_2} + 2\ C_2H_5OH \xrightarrow{C_2H_5ONa}$$

$$2\ CH_3Si(OC_2H_5)_3 + H_2$$

Similarly, dimethyldiethoxysilane (77%) and methyltriethoxysilane (69%) were obtained from compound VII.

$$\underset{\text{VII}}{(CH_3)_2(C_2H_5O)SiSi(CH_3)(OC_2H_5)_2} + 2\ C_2H_5OH \xrightarrow{C_2H_5ONa}$$

$$(CH_3)_2Si(OC_2H_5)_2 + CH_3Si(OC_2H_5)_3 + H_2$$

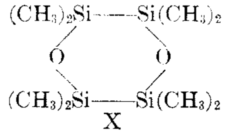
When compound VI or VII alone, or a mixture of both, was allowed to react with an appropriate quantity of methylmagnesium bromide, there were usually obtained two major products, pentamethylethoxydisilane (VIII) and 1,1,2,2-tetramethyl-1,2-diethoxydisilane (IX). The structure of the latter compound was confirmed by its conversion to the dichloride, difluoride, and hydrolysis product, as described below.

Compounds VIII and IX were converted in satisfactory yields to pentamethylchlorodisilanes (I) and 1,1,2,2-tetramethyl-1,2-dichlorodisilane (III), respectively, through the reaction either with acetyl chloride or with benzoyl chloride according to the procedure of Ladenburg,[24] and to pentamethylfluorodisilane (II) and 1,1,2,2-tetramethyl-1,2-difluorodisilane (IV), respectively, by treating them with aqueous hydrogen fluoride in the manner of Marans, Sommer, and Whitmore.[25] Chlorides and fluorides thus obtained were in satisfactory agreement with the corresponding compounds derived by the alternative route, Method I.

Of these two methods, Method I now seems to offer a better approach to the preparation of compounds having the formulas, $(CH_3)_3SiSi(CH_3)_2X$ and $(CH_3)_2XSiSi(CH_3)_2X$, X being chlorine and fluorine. Method II might suffer, though not seriously, from purity limitations of compounds imposed by the absence of any step which thoroughly eliminates the possible contamination by disiloxanes.

It was hoped that the controlled hydrolysis of compounds $(CH_3)_2XSiSi(CH_3)_2X$ would lead to the formation of the corresponding diol; however, a cyclic dimer, 2,2,3,3,5,5,6,6-octamethyl-1,4-dioxa-2,3,5,6-tetrasilacyclohexane (X), was the product.

$$2\ (CH_3)_2XSiSi(CH_3)_2X \xrightarrow{H_2O}$$



X

EXPERIMENTAL

All temperatures reported here are uncorrected. The higher-boiling residue of methylchlorosilanes was supplied by the Tokyo-Shibaura Elec. Co., Ltd. The disilane fraction was obtained by fractional distillation of the residue through a 1.3 cm. × 100 cm. Fenske column.

PREPARATION BY METHOD I

Hexamethyldisilane. This compound was prepared in substantially the same manner as that reported previously, b.p. 112°, m.p. 11°, n_D^{20} 1.4228, d_4^{20} 0.7265, in yields of 50–70%. A boiling point of 113°, m.p. 14°, $n_D^{24.4}$ 1.4207, $d_4^{24.4}$ 0.7230 has been reported for hexamethyldisilane.[2]

Pentamethylchlorodisilane (I). A 300-ml. three-necked flask was fitted with an air-tight stirrer, a thermometer, and an ice water-containing cold-finger which was connected to an apparatus for collecting gas. In the flask were placed 30 g. (0.21 mole) of hexamethyldisilane and 109 g. of concentrated sulfuric acid of *sp. gr.* 1.84. The mixture was vigorously stirred at about 22°. The reaction began at once as evidenced by the evolution of gas. After 3.5 hours 5 l. of methane was collected and the reaction mixture appeared to be a homogeneous solution; stirring then was discontinued. At that time the mixture was cooled with an ice-bath and 16 g. (0.30 mole) of dry pulverized ammonium chloride was added to the mixture over 30 minutes with stirring.

Stirring was continued for an additional 30 minutes. Separation followed by simple distillation of the organic layer gave 28 g. of the crude chloride which distilled over a range up to 150°. A second run carried out in a 500-ml. flask using identical quantities of materials yielded 57 g. of the crude product. The crude distillates from the two runs were combined and redistilled through a modified Stedman column rated at about 20 theoretical plates to give: (a) trimethylchlorosilane, b.p. 57–60°, 3 g.

Anal. Calc'd for C_3H_9ClSi: Cl, 32.7. Found: Cl, 32.8.

(b) Pentamethylchlorodisilane, b.p. 134–135°, n_D^{20} 1.4430, d_4^{20} 0.8684, 65 g., yield 64%.

Anal. Calc'd for $C_5H_{15}ClSi_2$: Cl, 21.3; M.R.,[26] 50.74. Found: Cl, 21.1, 21.5; M.R., 50.94.

Pentamethylfluorodisilane (II). The procedure was the same as that described in the preceding paragraph for pentamethylchlorodisilane except that 36 g. (0.24 mole) of hexamethyldisilane and 125 g. of concentrated sulfuric acid were stirred at 25°, and after evolution of 6 l. of methane (2.5 hours) 18 g. (0.49 mole) of ammonium fluoride was allowed to react. Fractionation gave: (a) Trimethylfluorosilane, b.p. 16–17°, 2 g. and (b) pentamethylfluorodisilane, b.p. 102°. n_D^{20} 1.4031, d_4^{20} 0.8083, 25 g., yield 72%.

Anal. Calc'd for $C_5H_{15}FSi_2$: F, 12.6; M.R., 45.33. Found: F, 12.7; M.R., 45.58.

1,1,2,2-Tetramethyl-1,2-dichlorodisilane (III). In a similar apparatus to that described in the preceding paragraphs there were placed 30 g. (0.21 mole) of hexamethyldisilane and 195 g. of concentrated sulfuric acid, and the mixture was vigorously stirred at 23°. First 5 l. (0.22 mole) of methane was evolved in 2.5 hours. At that time the apparent rate of gas evolution suddenly decreased to less than one-tenth that of the initial rate although the reaction mixture had become homogeneous. After two days of standing the total volume of gas evolved amounted to 9.6 l. (93%). The reaction mixture then was treated with 32 g. (0.59 mole) of ammonium chloride and worked up as above to give 32 g. of a crude dichloride distilling over a range up to 150°.

In a second run the above experiment was repeated but 50 g. (0.34 mole) of hexamethyldisilane, 325 g. of concentrated sulfuric acid, and 54 g. (1.0 mole) of ammonium chloride were used. From this run 51 g. of the crude product was obtained.

Fractional distillation of the combined crude dichloride from the two runs yielded: (a) trimethylchlorosilane, b.p. 58°, 7.0 g.; and (b) 1,1,2,2-tetramethyl-1,2-dichlorodisilane, b.p. 148°, n_D^{20} 1.4545, d_4^{20} 1.0103, 55 g., yield 55%.

Anal. Calc'd for $C_4H_{12}Cl_2Si_2$: Cl, 37.9; M.R., 50.30. Found: Cl, 37.9, 37.9; M.R., 50.67.

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(24) Ladenburg, *Ann.*, **164,** 300 (1872).

(25) Marans, Sommer, and Whitmore, *J. Am. Chem. Soc.*, **73,** 5127 (1951).

(26) Molar refractions were calculated by the method of Vogel, Cresswell, and Leicester, *J. Phys. Chem.*, **58,** 174 (1954).

1,1,2,2-Tetramethyl-1,2-difluorodisilane (IV). This reaction was run in the same manner as that for compound III, except that 48 g. (0.33 mole) of hexamethyldisilane was allowed to react with 350 g. of concentrated sulfuric acid at 30°, and after 48 hours of stirring 50 g. (1.4 moles) of ammonium fluoride was added to the sulfuric acid solution. Fractionation of the organic layer which resulted gave the following products: (a) trimethylfluorosilane, b.p. 16–17°, 4 g.; and (b) 1,1,2,2-tetramethyl-1,2-difluorodisilane, b.p. 92–93°, n_{D}^{20} 1.3837, d_4^{20} 0.9120, 33 g., yield 64%.

Anal. Calc'd for $C_4H_{12}F_2Si_2$: F, 24.6; M.R., 39.48. Found: F, 24.6; M.R., 39.52.

1,1,2,2-Tetramethyl-1-chloro-2-fluorodisilane (V). In accordance with the procedure described above 15.5 l. of methane was evolved and the sulfuric acid solution was obtained from 48 g. (0.33 mole) of hexamethyldisilane and 350 g. of concentrated sulfuric acid. A mixture of 22 g. (0.41 mole) of ammonium chloride and 15 g. (0.41 mole) of ammonium fluoride then was added to the solution. The organic layer was separated and submitted to fractional distillation to afford the following three expected compounds in addition to 2 g. of trimethylfluorosilane: (a) 1,1,2,2-tetramethyl-1,2-difluorodisilane, b.p. 92°, 9 g., yield 18%; (b) 1,1,2,2-tetramethyl-1,2-dichlorodisilane, b.p. 147°, 4.5 g., yield 7.3%; and (c) 1,1,2,2-tetramethyl-1-chloro-2-fluorodisilane, b.p. 120°, n_{D}^{20} 1.4201, d_4^{20} 0.9623, 16 g., yield 28%.

Anal. Calc'd for $C_4H_{12}ClFSi_2$: Neut. equiv., 85.4; Cl, 20.8; M.R., 44.89. Found: Neut. equiv., 85.3; Cl, 20.7; M.R., 44.87.

PREPARATION BY METHOD II

1,2-Dimethyl-1,1,2,2-tetraethoxydisilane (VI) and *1,1,2-trimethyl-1,2,2-triethoxydisilane.* In a 2-l. three-necked flask provided with an air-tight mechanical stirrer, a dropping-funnel the stem of which extended into the liquid nearly to the bottom of the flask, and an efficient reflux condenser was added slowly, with external cooling and vigorous stirring, 430 g. of absolute ethanol to 600 g. of a disilane fraction (b.p. 155–160°; hydrolyzable chlorine content, 55.2%). The reaction system was kept under reduced pressure (40–50 mm.) by means of an aspirator during and after the addition of ethanol so as to remove the hydrogen chloride generated as quickly as possible. Then 800 ml. of absolute ether was added to the mixture and dry ammonia gas was passed through a gas inlet tube which had been fitted in place of the dropping-funnel, until a test with *p*H paper indicated the ether solution to be slightly alkaline. This took about 11 hours. After an additional 6 hours of stirring the mixture was filtered. The filtrate and several portions of ether washings were combined, the ether was distilled off, and the residue was submitted to fractional distillation under reduced pressure through a 1.3 cm. × 100 cm. Fenske column to give the following fractions: (a) b.p. 47–90° (26 mm.), 60 g.; (b) 90–91° (26 mm.), 64 g.; (c) 91–104° (26 mm.), 35 g.; (d) 104–108° (28 mm.), 230 g.; and higher-boiling residue, 86 g.

Redistillation of fraction (b) in a 1.0 cm. × 50 cm. Stedman-typed column gave 46 g. of 1,1,2-trimethyl-1,2,2-triethoxydisilane, b.p. 85.5–87° (21 mm.), n_{D}^{20} 1.4220, d_4^{20} 0.8873.

Anal.[27] Calc'd for $C_9H_{24}O_3Si_2$: Si, 23.8; M.R., 67.52. Found: Si, 24.2; M.R., 67.68.

A part of fraction (b) was redistilled in the same column as above to give 1,2-dimethyl-1,1,2,2-tetraethoxydisilane, b.p. 101.5–102° (22 mm.), n_{D}^{20} 1.4200, d_4^{20} 0.9282.

Anal. Calc'd for $C_{10}H_{26}O_4Si_2$: Si, 21.1; M.R., 72.97. Found: Si, 21.4; M.R., 72.61.

In a second run using pyridine as the hydrogen chloride-acceptor, 14 g. of 1,1,2-trimethyl-1,2,2-triethoxydisilane, b.p. 72–73° (13 mm.), d_4^{20} 0.889, was obtained from 64 g. of a disilane fraction (b.p. 154–159°, Cl, 48.9%).

Anal. Calc'd for $C_9H_{24}O_3Si$: C, 45.76; H, 10.23; Si, 23.8. Found: C, 45.60; H, 10.07; Si, 23.9.

An estimation of the hydrogen evolved by the action of an alkali on compounds VI and VII was carried out using the Zerewitinoff apparatus. 1,2-Dimethyl-1,1,2,2-tetraethoxydisilane evolved about 99% of the theory of hydrogen upon mixing with 0.2 *N* sodium *n*-butoxide in *n*-butanol at room temperature (20°), while samples of 1,1,2-trimethyl-1,2,2-triethoxydisilane gave only 83% of the theory of hydrogen even on treatment with 1.5 *N* sodium *n*-butoxide at 80°.

Cleavage of compounds VI *and* VII *by ethanol in the presence of sodium ethoxide.* Sodium (0.1 g., 0.004 g.-atom) was dissolved in 8.0 g. (0.175 mole) of absolute ethanol. To the stirred solution contained in a 100-ml. flask equipped with an efficient reflux condenser and a dropping-funnel was added 20 g. (0.075 mole) of 1,2-dimethyl-1,1,2,2-tetraethoxydisilane in portions. An energetic evolution of hydrogen took place. After the addition had been completed, the reaction mixture was allowed to stand overnight, then was heated to reflux for 2.5 hours. Fractionation in a 1.0 cm. × 30 cm. Stedman column gave 24 g. (91%) of methyltriethoxysilane, b.p. 141.5–144°, n_{D}^{20} 1.3841. (Literature:[28] b.p. 143°, n_4^{20} 1.3835).

Neither dimethyldiethoxysilane (b.p. 113.5°) nor tetraethoxysilane (b.p. 168°) was isolated.

By the same procedure as above, 30 g. (0.13 mole) of 1,1,2-trimethyl-1,2,2-triethoxydisilane was allowed to react with 13 g. (0.28 mole) of absolute ethanol in the presence of about 0.004 mole of sodium ethoxide. After 6 hours of reflux the reaction mixture was distilled to give the following two compounds in an approximately equimolar proportion: (a) 14.5 g. (0.10 mole) of dimethyldiethoxysilane, b.p. 112°, n_{D}^{20} 1.3850 (literature[29] b.p. 113.5°, n_{D}^{20} 1.3810), yield 77%; and (b) 15.5 g. (0.09 mole) of methyltriethoxysilane, b.p. 142°, n_{D}^{20} 1.3863 (literature[28] b.p. 143°, n_{D}^{20} 1.3835), yield 69%. No trimethylethoxysilane–ethanol azeotrope, b.p. 66°, was obtained, although about 5 ml. of an ethanol fraction, b.p. 78°, was recovered, presumably containing a somewhat small quantity of dimethyldiethoxysilane.

Pentamethylethoxydisilane (VIII) *and 1,1,2,2-tetramethyl-1,2-diethoxydisilane* (IX). To a solution containing 180 g. (0.68 mole) of 1,2-dimethyl-1,1,2,2-tetraethoxydisilane in 600 ml. of dry ether was added dropwise, with cooling and stirring, a solution of methylmagnesium bromide which had been prepared from 43 g. (1.8 g. of atoms) of magnesium in 700 ml. of ether. The reaction mixture was warmed to reflux for several hours and then was cooled and filtered. The ether was distilled off from the filtrate leaving 100 g. of a colorless liquid residue. Fractional distillation in a 1.0 cm. × 50 cm. Stedman column gave only two fractions: (a) pentamethylethoxydisilane, b.p. 143.5–144.5°, n_{D}^{20} 1.4229, d_4^{20} 0.7993, 58 g., yield 49%.

Anal. Calc'd for $C_7H_{20}OSi_2$: Si, 31.9; M.R., 56.63. Found: Si, 31.5; M.R., 56.13. and (b) 1,1,2,2-tetramethyl-1,2-diethoxydisilane, b.p. 169–170°, n_{D}^{20} 1.4240, d_4^{20} 0.8507, 12 g., yield 8.5%.

Anal. Calc'd for $C_8H_{22}O_2Si_2$: Si, 27.2; M.R., 61.96. Found: Si, 27.1; M.R., 61.89.

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(27) The silicon analyses were made according to the procedure of Nozakura at Osaka University (personal communication), which consisted of this sequence of operations: digestion of a weighed sample with concentrated sulfuric acid in a sealed hard glass tube at 100–150° for one hour; transference of the resultant sulfuric acid solution to a crucible with the aid of several small portions of sulfuric acid; placing the crucible on a hot plate and heating until fumes of sulfur trioxide were evolved; and finally ignition of the residue to constant weight.

(28) Fretcher and Hunter, *J. Am. Chem. Soc.*, **71**, 2922 (1949).

(29) Fletcher and Hunter, *J. Am. Chem. Soc.*, **71**, 2918 (1949).

In a second run, using 68 g. (0.28 mole) of 1,1,2-trimethyl-1,2,2-triethoxydisilane and 0.3 mole of methylmagnesium bromide, there was prepared 19 g. (32%) of 1,1,2,2-tetramethyl-1,2-diethoxydisilane, b.p. 169, d_4^{20} 0.8499.

In a third run a solution containing 2 moles of methylmagnesium bromide in 1.3 l. of ether was added to 267 g. of an ethanolysis product of a disilane fraction which had not been rectified but was subjected only to simple distillation over the range 75–140° (24 mm.). The reaction mixture then was worked up as above; and finally, there was obtained 52 g. of pentamethylethoxydisilane, b.p. 143–145°, and 81 g. of 1,1,2,2-tetramethyl-1,2-diethoxydisilane, b.p. 168–170°.

Pentamethylchlorodisilane (I). A mixture of 46 g. (0.26 mole) of pentamethylethoxydisilane and 22.5 g. (0.29 mole) of acetyl chloride was heated at 104–110° for one hour in a sealed glass tube. Five days later the reaction mixture was fractionally distilled to give 24 g. (80%) of pentamethylchlorodisilane, b.p. 135.5–137°, n_D^{20} 1.4430, d_4^{20} 0.8680, as well as 25 g. ethyl acetate.

Anal. Calc'd for $C_5H_{15}ClSi_2$: Cl, 21.3; M.R., 50.74. Found: Cl, 21.5; M.R., 50.90.

In a second run the procedure was similar to that just described except that 28 g. (0.16 mole) of pentamethylethoxydisilane and 24 g. (0.17 mole) of benzoyl chloride were brought into reaction at 235–240° for 4 hours in the presence of a few drops of pyridine. Crude pentamethylchlorodisilane, b.p. 130–135°, weighing 19 g. (71%), was obtained.

A third experiment, using 20 g. (0.11 mole) of pentamethylethoxydisilane and 17 g. (0.12 mole) of benzoyl chloride, but without pyridine, afforded 15 g. (82%) of crude pentamethylchlorodisilane.

Crude products from these two runs were combined and redistilled through a 0.8 cm. × 120 cm. Fenske column to give 20 g. of a pure sample, b.p. 134.5–136°.

Anal. Calc'd for $C_5H_{15}ClSi_2$: Cl, 21.3. Found: Cl, 21.6.

1,1,2,2-Tetramethyl-1,2-dichlorodisilane (III). This compound was prepared in the same manner as that above using 15 g. (0.073 mole) of 1,1,2,2-tetramethyl-1,2-diethoxydisilane, 21 g. (0.15 mole) of benzoyl chloride, and a few drops of pyridine, and heating the mixture to 230–240° for 4.5 hours. Distillation yielded 12 g. (90%) of the crude dichloride, b.p. 140–153°. The same procedure was repeated but 23 g. (0.11 mole) of 1,1,2,2-tetramethyl-1,2-diethoxydisilane, 33 g. (0.23 mole) of benzoyl chloride, and two drops of pyridine were used. In this run a small amount of an unidentified low-boiling product was found to be formed, and the crude dichloride weighed only 13 g. (64%).

Redistillation of the combined liquid from the two runs gave 25 g. of 1,1,2,2-tetramethyl-1,2-dichlorodisilane, b.p. 146.5–148°, n_D^{20} 1.4565, d_4^{20} 1.010.

Anal. Calc'd for $C_4H_{12}Cl_2Si_2$: Cl, 37.9. Found: Cl, 37.3.

Pentamethylfluorodisilane (II). Following a procedure of Marans, Sommer, and Whitmore,[25] a mixture of 20 g. (0.11 mole) of pentamethylethoxydisilane and 15 g. (0.3 mole) of 47% aqueous hydrogen fluoride was stirred for 3 hours in a 1-l. copper flask with external cooling by means of an ice-bath. The organic layer was separated and then was fractionated to give 11 g. (65%) of pentamethylfluorodisilane, b.p. 102°, n_D^{20} 1.4028, d_4^{20} 0.811.

Anal. Calc'd for $C_5H_{15}FSi_2$: F, 12.6; M.R., 45.33. Found: F, 12.7; M.R., 45.19.

1,1,2,2-Tetramethyl-1,2-difluorodisilane (IV). In quite a similar manner to that just described there was prepared from 17 g. (0.083 mole) of 1,1,2,2-tetramethyl-1,2-diethoxydisilane and 31 g. of 47% aqueous hydrogen fluoride, 7.7 g. (61%) of 1,1,2,2-tetramethyl-1,2-difluorodisilane, b.p. 92°, n_D^{20} 1.3821, d_4^{20} 0.919.

Anal. Calc'd for $C_4H_{12}F_2Si_2$: F, 24.6; M.R., 39.48. Found: F, 25.4; M.R., 39.05.

HYDROLYSIS OF $(\mathrm{CH_3})_2\mathrm{XSiSi}(\mathrm{CH_3})_2\mathrm{X}$

2,2,3,3,5,5,6,6-Octamethyl-1,4-dioxa-2,3,5,6-tetrasilacyclohexane (X). This compound was prepared from the difunctional disilanes by a hydrolysis which was carried out in the hope of preparing the disilanediol, using three different procedures according to the disilanes used.

When 5.2 g. (0.035 mole) of the difluorodisilane, which had been prepared by Method II, was shaken with excess dilute alkali in the cold, a solid organic phase resulted. Filtration of this phase yielded 2.7 g. (57%) of white crystals, which upon recrystallization from aqueous ethanol had a m.p. of 45°, and proved to be the cyclic dimer (X).

Anal. Calc'd for $C_8H_{24}O_2Si_4$: C, 36.32; H, 9.15; Si, 42.5; Mol. wt., 265.6. Found: C, 36.20; H, 9.07; Si, 42.4; Mol. wt., 263 (cryoscopic in benzene).

The technique for the controlled hydrolysis of dichlorodisilane was in accordance with that of Okawara, Hashitani, and Watase[30] for the synthesis of diallylsilanediol. A saturated sodium chloride solution containing an excess of solid sodium chloride (100 ml.) and 100 ml. of ether were placed in a 500-ml. flask equipped with a mechanical stirrer and surrounded by an ice-salt cooling bath. Then Methyl Orange indicator was added. A solution of 10 g. (0.053 mole) of 1,1,2,2-tetramethyl-1,2-dichlorodisilane in 100 ml. of dry ether was slowly added from a dropping-funnel with rapid stirring. The hydrogen chloride generated was neutralized with 1 *N* sodium hydroxide. The addition of the dichlorodisilane and the alkaline solution was adjusted so that the color change of the Methyl Orange was between a slight red and orange. During the reaction the temperature was maintained below 5°. After the addition was completed, the ether layer was separated and dried over sodium sulfate. Then the ether was evaporated leaving an oil most of which easily solidified on cooling with ice-water. Filtration gave 4.8 g. (70%) of crystals and 1.7 g. of oily matter. A recrystallized sample had m.p. 44°. The infrared spectrum showed no O—H absorption.

The hydrolysis of 1,1,2,2-tetramethyl-1,2-diethoxydisilane was performed after the procedure of Hyde.[31] A mixture of 10 g. (0.048 mole) of the diethoxydisilane and 3.5 g. (0.19 mole) of distilled water was placed in an Erlenmeyer flask and was kept at 25° over 80 hours with intermittent shaking. Two liquid phases were still present at that time, but a white mass of crystals appeared on cooling to 0°. Filtration of the cold mixture gave 1.8 g. (27%) of $[—(CH_3)_2SiSi(CH_3)_2—O—]_2$, m.p. 45°, as well as 3 g. of an oily product.

Acknowledgments. The authors wish to express their appreciation to Professor Minoru Imoto for his continued interest in the present investigation. They are also indebted to the Tokyo-Shibaura Elec. Co., Ltd. for a generous gift of the methylchlorosilane residue and for financial assistance.

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(30) Okawara, Hashitani, and Watase, *Bull. Chem. Soc. Japan*, **26**, 279 (1953).

(31) Hyde, *J. Am. Chem. Soc.*, **75**, 2166 (1953).