THE SYNTHESIS AND REACTIONS OF CERTAIN DISILANES CONTAINING CHLOROMETHYL GROUPS

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Although a large number of organofunctional silicon compounds are known, disilanes with functional groups in the organic portion of the molecules have only been scantily considered.

In a previous paper[1] we reported the synthesis and intramolecular rearrangement of the first two disilanes containing a chloromethyl group: (chloromethyl)pentamethyldisilane (I) and 1-(chloromethyl)-2-chlorotetramethyldisilane.

As an extension of the previous work, we have now prepared two further organodisilanes with chlorine in the side chain, (dichloromethyl)pentamethyldisilane (II) and 1,2-bis(chloromethyl)tetramethyldisilane (III), and have investigated some of their reactions. A further study of the chemical behavior of compound (I) has also been made.

Compound (II) was prepared by the reaction of methylmagnesium bromide with a fraction corresponding to dichlorinated methylchlorodisilanes, which had been obtained, as described previously, by photochemical chlorination in the liquid phase of the disilane fraction*.

$$(CH_3)_nCl_{6-n}Si_2 \xrightarrow[\text{UV light}]{Cl_2} Cl_2CH(CH_3)_{n-1}Cl_{6-n}Si_2 \xrightarrow{CH_3MgBr} \underset{\text{(II)}}{Cl_2CH(CH_3)_2SiSi(CH_3)_3} \quad (1)$$

Treatment of the product with sodium ethoxide in absolute ethanol gave the known ethoxypentamethyldisilane in 57% yield and methylene chloride in 72% yield. The pentamethyldisilanyl moiety was also partly recovered in the form of the oxide $[(CH_3)_3SiSi(CH_3)_2]_2O$. This observation provides good evidence for structure (II).

$$(CH_3)_3SiSi(CH_3)_2CHCl_2 + C_2H_5OH \xrightarrow{NaOC_2H_5} (CH_3)_3SiSi(CH_3)_2OC_2H_5 + CH_2Cl_2$$

Similar cleavages of dichloromethyl groups from silicon by basic reagents have been described in the literature[2]. The result of the intramolecular rearrangement of compound (II) with anhydrous aluminum chloride, which will be described below, is also in good agreement with the structure (II).

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* The disilane fraction refers to a fraction boiling over the range of about 150–160°, which is obtained by fractionation of the higher-boiling fraction of methylchlorosilanes produced by the so-called "direct synthesis". It is composed mainly of $CH_3Cl_2SiSiCH_3Cl_2$ and $(CH_3)_2ClSiSiCH_3Cl_2$, somewhat contaminated by siloxanes.

Compound (III) must also have been formed in reaction 1, but could not be isolated in a pure state. This substance was successfully synthesized by the peroxide-catalyzed chlorination of compound (I) with sulfuryl chloride.

$$\mathrm{ClCH_2(CH_3)_2SiSi(CH_3)_3} \xrightarrow[(C_6H_5CO_2)_2]{SO_2Cl_2} \underset{(III)}{\mathrm{ClCH_2(CH_3)_2SiSi(CH_3)_2CH_2Cl}} \qquad (2)$$

The yield was 35 % on the basis of unrecovered (I); compound (II) was also obtained during the fractional distillation of the reaction product (13 % yield). In contrast to the analogous reaction of hexamethyldisilane[1], cleavage of the silicon–silicon bond was found to be insignificant.

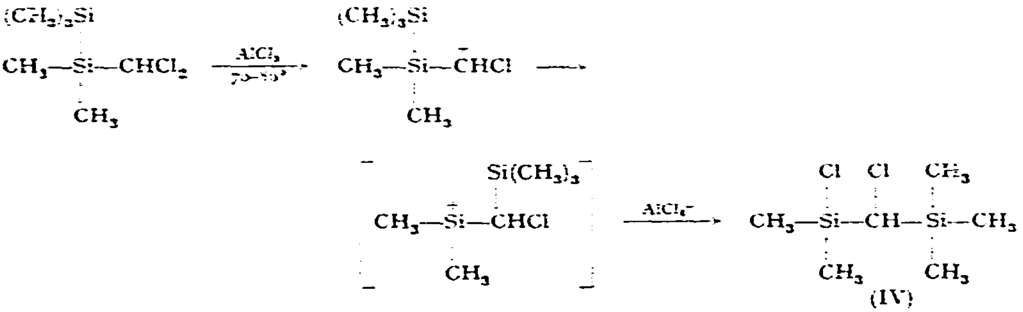
It has been reported in the literature[3,4] that the chloromethyl group attached to silicon can easily be cleaved by the action of potassium cyanide in alcohols. In agreement with this, we have now obtained ethoxypentamethyldisilane in 84 % yield from compound (I) and potassium cyanide in ethanol. This reaction was applied to compound (III) for its structure-proof, and the known 1,2-diethoxytetramethyldisilane was, indeed, obtained on treatment of (III) with sodium cyanide and with potassium cyanide in absolute ethanol, though in rather poor yields (24 and 34 %, respectively).

No cyanomethyl intermediates were isolated.

$$\mathrm{ClCH_2(CH_3)_2SiSi(CH_3)_2CH_2Cl + 2KCN\ (or\ NaCN)} \longrightarrow \mathrm{[NCCH_2(CH_3)_2SiSi(CH_3)_2CH_2CN]}$$

$$\xrightarrow{C_2H_5OH} \mathrm{C_2H_5O(CH_3)_2SiSi(CH_3)_2OC_2H_5 + 2CH_3CN}$$

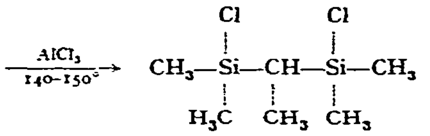
(Dichloromethyl)pentamethyldisilane (II) was found to undergo two successive and discrete intramolecular rearrangements with anhydrous aluminum chloride. Under mild conditions, *i.e.*, at a reaction temperature of 70–80°, only migration of the trimethylsilyl group from silicon to carbon took place to give (trimethylsilyl)(chlorodimethylsilyl)chloromethane (IV) in 83 % yield.



$$\mathrm{CH_3{-}\overset{(CH_3)_3Si}{\underset{CH_3}{Si}}{-}CHCl_2} \xrightarrow[70\text{–}80°]{AlCl_3} \mathrm{CH_3{-}\overset{(CH_3)_3Si}{\underset{CH_3}{Si}}{-}\overset{-}{C}HCl} \longrightarrow$$

$$\left[\mathrm{CH_3{-}\underset{CH_3}{\overset{+}{Si}}{-}\overset{Si(CH_3)_3}{CHCl}}\right]^- \xrightarrow{AlCl_4^-} \underset{(IV)}{\mathrm{CH_3{-}\overset{Cl}{\underset{CH_3}{Si}}{-}\overset{Cl}{CH}{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}CH_3}}$$

By raising the reaction temperature to 140–150° and employing a larger amount of the catalyst, the second intramolecular rearrangement, which involved the migration of a methyl group from silicon to carbon, was effected and gave 1,1-bis(chlorodimethylsilyl)ethane (V) in overal yields of about 70 %.



$$(\mathrm{IV}) \xrightarrow[140\text{–}150^{\circ}]{AlCl_3} CH_3\text{—}\overset{Cl}{\underset{H_3C}{Si}}\text{—}\underset{CH_3}{CH}\text{—}\overset{Cl}{\underset{CH_3}{Si}}\text{—}CH_3 \quad (\mathrm{V})$$

Compounds (IV) and (V) did not react with bromine, thus indicating the complete disappearance of the original silicon–silicon bonds in the molecules*. They were methylated with the Grignard reagent to afford bis(trimethylsilyl)chloromethane

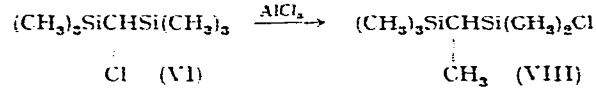
$$(CH_3)_3SiCHClSi(CH_3)_3 \quad (\mathrm{VI})$$

and 1,1-bis(trimethylsilyl)ethane

$$(CH_3)_3SiCH(CH_3)Si(CH_3)_3 \quad (\mathrm{VII})$$

respectively. These two compounds, obtained through other routes, have already been described in the literature[5,6,7] and it has been shown that the physical constants of our products are in reasonable agreement with the reported values.

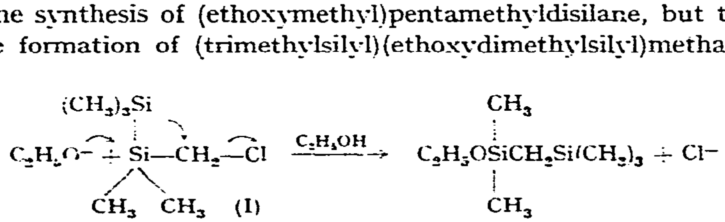
Compound (VI) has also been found to undergo a similar intramolecular rearrangement to that described for compound (IV), giving 1-(trimethylsilyl)-1-(chlorodimethylsilyl)ethane (VIII) in 60 % yield.



$$\underset{Cl\quad(\mathrm{VI})}{(CH_3)_3SiCHSi(CH_3)_3} \xrightarrow{AlCl_3} \underset{CH_3\quad(\mathrm{VIII})}{(CH_3)_3SiCHSi(CH_3)_2Cl}$$

Incidentally, it is very interesting to compare our results with those of Sommer and his co-workers[8] who observed that in the presence of anhydrous aluminum chloride both (dichloromethyl)trimethylsilane and (α-chloroethyl)trimethylsilane undergo extensive cleavage of the silicon–carbon bond with the formation of ethylene, in addition to the intramolecular rearrangement. Doubtless, the impossibility or great difficulty of forming a compound $CH_3CH{=}Si(CH_3)_2$** is responsible for the much better yields of rearrangement products in our case.

Nucleophilic intramolecular rearrangements involving silicon have been reported for (chloromethyl)aryldimethylsilane[10] and (chloro- and iodomethyl)dimethylsilanes[11] An additional example has now been obtained in the reaction of (chloromethyl)pentamethyldisilane (I) with sodium ethoxide in absolute ethanol. The initial aim of the reaction was the synthesis of (ethoxymethyl)pentamethyldisilane, but the reaction resulted in the formation of (trimethylsilyl)(ethoxydimethylsilyl)methane in 72 % yield.



The chloromethyl group of compound (I) could be converted into an iodomethyl

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* See the footnote of ref. 1.

** No compound containing a double bond to silicon is known. See, for example, ref. 9.

group by means of sodium iodide in dry acetone, giving (iodomethyl)pentamethyldisilane $ICH_2(CH_3)_2SiSi(CH_3)_3$ (IX) in 77 % yield. A similar reaction was successfully carried out with compound (III); 1,2-bis(iodomethyl)tetramethyldisilane

$$ICH_2(CH_3)_2SiSi(CH_3)_2CH_2I \quad (X)$$

was obtained in 75 % yield.

Both (chloromethyl)pentamethyldisilane and (iodomethyl)pentamethyldisilane reacted smoothly with magnesium in ether to give the corresponding Grignard reagents in 79 and 40 % yields, respectively. Pentamethyldisilanylmethylmercuric chloride (XI) was obtained, in 62 % yield, by the reaction of the former Grignard reagent with mercuric chloride.

$$(CH_3)_3SiSi(CH_3)_2CH_2Cl \xrightarrow[\text{ether}]{\text{Mg}} (CH_3)_3SiSi(CH_3)_2CH_2MgCl \xrightarrow{HgCl_2}$$
$$(CH_3)_3SiSi(CH_3)_2CH_2HgCl$$
$$(XI)$$

EXPERIMENTAL

All boiling and melting points reported here are uncorrected. Silicon analyses were carried out as described previously[12]. Analyses for chlorine bonded to carbon were performed following the procedures reported by Peel, Clark and Wagner[13].

(Chloromethyl)pentamethyldisilane (I)

This compound was prepared in essentially the same manner as that reported previously[1], except that the preparation was carried out on a much larger scale. The product had b.p. 52° at 10 mm and m.p. 22–23.5°. The melting point reported previously[1] is 6–7°. Probably the previous sample was slightly contaminated with siloxanes, although analytical results for silicon were in good agreement with theory. The present product was analyzed for carbon, hydrogen and chlorine. (Found: C, 39.87; H, 9.56; Cl, 19.35. $C_6H_{17}ClSi_2$ calcd.: C, 39.86; H, 9.48; Cl, 19.61 %.)

(Dichloromethyl)pentamethyldisilane (II)

To a stirred solution of the Grignard reagent, prepared from 286 g (3.0 mole) of methyl bromide, 70 g (2.9 g-atoms) of magnesium turnings in 1 l of absolute ether, was added differentially 160 g of the higher-boiling fraction, or the dichlorination products, which had been obtained from the photochemical chlorination of the disilane fraction in accordance with the techniques reported previously[1]. The fraction corresponding to the dichlorination products boiled over the range 80–120° at 20 mm and contained 49.4 % of hydrolyzable chlorine. After completion of the addition, the reaction mixture was heated to reflux for 12 h. Then about 500 ml of ether was distilled off from the mixture. Hydrolysis with dilute hydrochloric acid was followed by separation of the organic layer, washing until neutral and drying over calcium chloride. Ether was removed on a steam bath. The residual oil was distilled under reduced pressure to give 85 g of a liquid boiling over the range 40–120° at 10 mm and 15 g of residue. The distillate was treated with cold concentrated sulfuric acid in order to remove completely any siloxane compounds. The organic layer was separated, diluted with

50 ml of ether, washed until neutral, dried over calcium chloride and then submitted to fractional distillation under reduced pressure through a 1.0 × 30 cm Stedman column to give the following two fractions: (1) (chloromethyl)pentamethyldisilane (I), 15 g, b.p. 51–53° at 10 mm, and (2) (dichloromethyl)pentamethyldisilane, 30 g, b.p. 72° at 10 mm, m.p. 23–24°, n_D^{20} 1.4740, d_4^{20} 1.0004, MR_D 60.89 (calcd. 60.49). (Found: C, 33.76; H, 7.63; Cl, 32.75; Si, 26.01. $C_6H_{16}Cl_2Si_2$ calcd.: C, 33.47; H, 7.49; Cl, 32.94; Si, 26.10 %.)

Reaction of (II) with ethanol in the presence of sodium ethoxide

Sodium (0.8 g, 0.035 g-atom) was dissolved in 15 g (0.33 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 28 g (0.13 mole) of compound (II) at room temperature over a 15-min period. The reaction mixture was heated to reflux for 30 min and then cautiously neutralized by introducing dry hydrogen chloride gas. At this point the reflux condenser was replaced by a descending cooler, and a lower-boiling product was distilled together with ethanol. Redistillation of the distillate through a 1.0 × 30 cm Stedman column gave 8 g (72 % yield) of methylene dichloride, b.p. 40°, d_4^{20} 1.3. The residue in the reaction vessel was filtered and washed with absolute ether. The filtrate and washings were combined and submitted to fractional distillation through the same column as above to give 13 g (57 % yield) of ethoxypentamethyldisilane, b.p. 141°, n_D^{20} 1.4250, d_4^{20} 0.7993 (literature[12]: b.p. 143.5–144.5°, n_D^{20} 1.4229, d_4^{20} 0.7993) and 4 g (22 % yield) of a liquid boling at 84–85° (9 mm) and having n_D^{20} 1.4405. This liquid was identical with pentamethyldisilanyl oxide $[(CH_3)_3SiSi(CH_3)_2]_2O$, b.p. 84° (9 mm), n_D^{20} 1.4395, which was obtained by hydrolysis of chloropentamethyldisilane. (Found: C, 43.52; H, 11.21; Si, 40.09. $C_{10}H_{30}OSi_4$ calcd.: C, 43.10; H, 10.85; Si, 40.32 %.)

1,2-Bis(chloromethyl)tetramethyldisilane (III)

This compound was prepared in essentially the same manner as that reported previously[1] for the preparation of compound (I) by the peroxide-catalyzed chlorination of hexamethyldisilane except that 60 g (0.33 mole) of (I) 49 g (0.36 mole) of sulfuryl chloride and 1 g of benzoyl peroxide were allowed to react at 110–120°. After completion of the reaction (15 h) the contents of the flask were first distilled under reduced pressure to give 61 g of a distillate boiling over the range 40–120° at 9 mm, together with 5 g of a low-boiling liquid, which presumably resulted from cleavage of the silicon–silicon bond, and which was collected in a trap at —78°. Redistillation of the main distillate in a 1.0 × 30 cm Stedman column gave the following three fractions: (1) recovered (I), b.p. 45–46° at 9 mm, n_D^{20} 1.4573, 12 g (20 % yield); (2) slightly impure (dichloromethyl)pentamethyldisilane (II), b.p. 63–65° at 9 mm, 9 g (13 % yield); (3) 1,2-bis(chloromethyl)tetramethyldisilane, b.p. 85° at 9 mm, m.p. 34°, 20 g [28 % yield on the basis of (I) employed]. The yield amounts to 35 % on the basis of unrecovered (I). (Found: C, 34.03; H, 7.60; Cl, 32.68; Si, 25.68. $C_6H_{15}Cl_2Si_2$ calcd.: C, 33.47; H, 7.49; Cl, 32.94; Si, 26.10 %.)

Reaction of (I) with sodium cyanide in ethanol

In a 250-ml three-necked flask fitted with a reflux condenser, dropping funnel and motor-driven stirrer there was placed 11 g (0.22 mole) of sodium cyanide and 30 g of absolute ethanol. To the stirred mixture was added dropwise 30 g (0.17 mole) of compound (I) at the reflux temperature of ethanol, and then heating and stirring was continued over a 15-h period. At this point the contents of the flask were cooled and filtered. The filtrate was fractionally distilled to give 19.5 g of ethoxypentamethyldisilane, b.p. 140°, n_D^{20} 1.4261, d_4^{20} 0.7992, MR_D 56.59 (calcd. 56.57), in 83 % yield. (Found: Si, 31.40. $C_7H_{20}OSi_2$ calcd.: Si, 31.84 %.)

Reaction of (III) with sodium cyanide in ethanol

Reaction of (III) (30 g, 0.14 mole) with sodium cyanide (20 g, 0.41 mole) in absolute ethanol (45 g) was carried out in the same manner as above. Fractionation gave 7 g of slightly impure 1,2-diethoxytetramethyldisilane, b.p. 165–169°, n_D^{20} 1.4259, d_4^{20} 0.8557 (literature[12], b.p. 169–170°, n_D^{20} 1.4240, d_4^{20} 0.8507), in 24 % yield. In addition, a relatively large amount (14 g) of unidentified higher-boiling fraction was formed.

Reaction of (III) with potassium cyanide in ethanol

In accordance with the techniques just described, 17 g (0.26 mole) of potassium cyanide and 25 g (0.12 mole) of (III) were caused to react in 50 g of absolute ethanol over a 50-h period. The reaction mixture was worked up as above to give 8 g of 1,2-diethoxytetramethyldisilane, b.p. 168–169°, n_D^{20} 1.4240, d_4^{20} 0.8530, in 34 % yield. There was also obtained 9 g of a higher-boiling fraction. (Found: Si, 26.81. $C_8H_{22}O_2Si_2$ calcd.: Si, 27.21 %.)

Intramolecular rearrangement of (II) with anhydrous aluminum chloride

A. Lower-temperature reaction. To 61 g (0.28 mole) of compound (II), stirred and protected from moisture, was added with cooling a small amount of anhydrous aluminum chloride. A vigorous, exothermic reaction took place. When the reaction subsided gentle heat was applied to the flask for a short period of time and then an additional small amount of the catalyst was introduced with cooling. These procedures were continued repeatedly until no further noticeable change occurred at the temperature of 70–80°. It was necessary to add a total of *ca.* 2.5 g of catalyst to complete the reaction. The reaction mixture was flash-distilled under reduced pressure to separate the product from aluminum chloride catalyst to give 55 g of a liquid boiling over the range of 90–100° at 25 mm. Fractionation of this catalyst-free distillate through a 1.0 × 30 cm Stedman column gave 50.5 g (82.8 %) of (trimethylsilyl)(chlorodimethylsilyl)chloromethane (IV), b.p. 76° at 12 mm, n_D^{20} 1.4595, d_4^{20} 1.0124, MR_D 58.19 (calcd. 58.10). [Found: Cl (bonded to silicon), 16.50. $C_6H_{16}Cl_2Si_2$ calcd.: Cl (bonded to silicon), 16.47 %.]

A sample of this compound did not react with bromine even on heating, indicating complete absence of silicon–silicon linkage in the molecule.

B. Higher-temperature reaction. To 40 g (0.186 mole) of (II) was added with stirring and cooling 0.7 g of anhydrous aluminum chloride. The reaction temperature was then carefully raised to 140–150°. At this temperature 4.4 g of the catalyst was added in small portions over a 2-h period. The reaction mixture was worked up in essentially the same manner as above. Fractionation of the catalyst-free distillate (32 g) gave 27 g of 1,1-bis(chlorodimethylsilyl)ethane (V), b.p. 77–78° at 14 mm, n_D^{20} 1.4607, d_4^{20} 1.0390, MR_D 57.09 (calcd. 57.41) in 68 % yield. [Found: Cl (bonded to silicon), 32.92. $C_6H_{16}Cl_2Si_2$ calcd.: Cl (bonded to silicon), 32.93 %.]

Bis(trimethylsilyl)chloromethane (*VI*)

To a solution containing 0.15 mole of methylmagnesium bromide was added 23 g (0.11 mole) of compound (IV). The reaction mixture was worked up in the usual manner. Fractional distillation gave 18 g (84% yield) of bis(trimethylsilyl)chloromethane (VI), b.p. 72–73° at 22 mm, n_D^{20} 1.4499, d_4^{20} 0.9041 (literature[5], b.p. 178.5° at 747 mm, n_D^{20} 1.4489, d_4^{20} 0.8900), MR_D 58,53 (calcd. 57.92). (Found: C, 42.56; H, 9.92; Si, 28.78. $C_7H_{17}ClSi_2$ calcd.: C, 43.13; H, 9.83; Si, 28.83%.)

1,1-Bis(trimethylsilyl)ethane (*VII*)

To a solution of 0.3 mole of methylmagnesium bromide in 120 ml of absolute ether was added 20 g (0.09 mole) of (V). After refluxing for a 12-h period, the reaction mixture was worked up in the usual manner. Fractionation gave 12 g (77% yield) of 1,1-bis(trimethylsilyl)ethane, b.p. 160–161°, n_D^{20} 1.4331, d_4^{20} 0.7797 (literature[6], b.p. 155.7° at 733 mm, n_D^{20} 1.4340, d_4^{20} 0.7821; literature[7], b.p. 158°, n_D^{20} 1.4332), MR_D 58.17 (calcd. 58.28). (Found: Si, 32.08. $C_8H_{22}Si_2$ calcd.: Si, 32.20%.)

Intramolecular rearrangement of (*VI*) *with anhydrous aluminum chloride*

To 35 g (0.18 mole) of (VI) was added 2 g of anhydrous aluminum chloride in small portions over a 4-h period at 100–140°. After a work-up as described above for the rearrangement of (II), there was obtained by fractional distillation 21 g of 1-(trimethylsilyl)-1-(chlorodimethylsilyl)ethane (VIII), b.p. 62°, at 12.5 mm, n_D^{20} 1.4462, d_4^{20} 0.8030, MR_D 57.84 (calcd. 58.23), in 60% yield. (Found: Cl, 17.91. $C_7H_{19}ClSi_2$ calcd.: Cl, 18.20%.)

Intramolecular rearrangement of (*I*) *with sodium ethoxide in ethanol*

Sodium (7 g, 0.3 g-atom) was dissolved in 50 g of absolute ethanol. To the stirred solution was added in portions a mixture of 38 g (0.21 mole) of (I) and 5 g of absolute ethanol at room temperature over a 1-h period. The reaction mixture was then heated to reflux for 5 h. Dry hydrogen chloride was introduced until the mixture became neutral against phenolphthalein. The formed sodium chloride was filtered off and washed with absolute ether. The filtrate and washings were combined and submitted to fractional distillation to give 29 g (72% yield) of (trimethylsilyl)(ethoxydimethylsilyl)methane, b.p. 159–160°, n_D^{20} 1.4183, d_4^{20} 0.8102 (literature[14], b.p. 159°, n_D^{20} 1.4183; literature[15], b.p. 161°, n_D^{25} 1.4148, d_4^{25} 0.8060), MR_D 59.28 (calcd. 59.07). (Found: Si, 29.21. $C_8H_{22}OSi_2$ calcd.: Si, 29.50%.)

In a second run, from the reaction of 50 g (0.28 mole) of (I) with 0.31 mole of sodium ethoxide in 50 g of ethanol there were obtained 10 g (19% yield) of (trimethylsilyl)(ethoxydimethylsilyl)methane, b.p. 160°, n_D^{20} 1.4180, and 19 g (44% yield) of its deetherated dimer, 1,3-bis(trimethylsilylmethyl)tetramethyldisiloxane $[(CH_3)_3SiCH_2Si(CH_3)_2]_2O$, b.p. 233–234°, n_D^{20} 1.4329, d_4^{20} 0.8352 (literature[16], b.p. 126° at 20 mm, n_D^{20} 1.4319, d_4^{20} 0.8311; literature[17], b.p. 93–94° at 3.5 mm, n_D^{20} 1.4340, d_4^{20} 0.8359), MR_D 94.85 (calcd. 95.46). [Found: Si, 36.31; mol. wt. (cryoscopic in benzene), 308. $C_{12}H_{34}OSi_4$ calcd.: Si, 36.62%; mol. wt. 307.]

No further study was made to pursue the cause of the formation of this dimeric substance.

(Iodomethyl)pentamethyldisilane (IX)

In a 1-l flask was placed 300 ml of dry acetone and 19.6 g (0.13 mole) of dry sodium iodide. To this solution there was added 18.1 g (0.1 mole) of (I). After refluxing for 20 h most of the acetone was distilled, and 300 ml of ether was then added. The precipitated sodium chloride was removed by dissolving it in water. The organic layer was separated, washed and dried over potassium carbonate. After removing the mixture of solvents, the residue was submitted to distillation under vacuum to give 26 g of a slightly yellow-colored liquid boiling at 93–97° (23 mm). This was shaken with a small amount of mercury. The resulting colorless oil was diluted with ether, and washed with a dilute solution of sodium bicarbonate, dried, and finally distilled. There was obtained 21 g of (iodomethyl)pentamethyldisilane, b.p. 96–97° (23 mm), n_D^{20} 1.5110. d_4^{20} 1.2675. MR_D 64.37 (calcd. 64.05). The yield was 77%. (Found: Si, 20.68. $C_6H_{17}ISi_2$ calcd.: Si, 20.64%.)

1,2-Bis(iodomethyl)tetramethyldisilane (X)

This compound was prepared in essentially the same manner as above except that 16 g (0.074 mole) of (III) and 22.5 g (0.15 mole) of dry sodium iodide were allowed to react in 300 ml of dry acetone for 15 h. There was obtained 20.5 g of (X), b.p. 104–105° (3 mm), n_D^{20} 1.5840, d_4^{20} 1.7264, MR_D 77.19 (calcd. 76.93), in 75% yield. (Found: Si, 14.08. $C_6H_{16}I_2Si_2$ calcd.: Si, 14.11%.)

Pentamethyldisilanylmethylmagnesium chloride $(CH_3)_3SiSi(CH_3)_2CH_2MgCl$

In a 100-ml three-necked flask fitted with a stirrer and reflux condenser there was placed 0.8 g (0.033 g-atom) of magnesium turnings, 5.0 g (0.028 mole) of (I) and 20 ml of dry ether. When a crystal of iodine was introduced and the mixture was warmed, the reaction set in very smoothly. When the reaction mixture had been maintained at gentle reflux with stirring for 2 h, the magnesium had practically disappeared to result in the formation of a transparent, grey solution. This solution was filtered through glass wool under nitrogen pressure and the reaction vessel was washed with several portions of dry ether. The filtrate and washings were combined and a pipetted sample was then titrated in the usual manner to determine the yield of the Grignard reagent. The yield of pentamethyldisilanylmethylmagnesium chloride was 79%.

Pentamethyldisilanylmethylmagnesium iodide, $(CH_3)_3SiSi(CH_3)_2CH_2MgI$

In the same manner as above there was allowed to react 0.5 g (0.021 g-atom) of magnesium turnings with 5.24 g (0.019 mole) of (IX) in 30 ml of dry ether. After a 4-h reflux there was obtained a white solution along with a fairly large amount of precipitated salt. At this point the mixture was filtered and then worked up as above The yield of pentamethyldisilanylmethylmagnesium iodide was 40%.

Pentamethyldisilanylmethylmercuric chloride (XI)

A solution of (pentamethyldisilanyl)methylmagnesium chloride was prepared from 5 g (0.028 mole) of (I) and 0.7 g (0.029 g-atom) of magnesium in 20 ml of dry ether. This solution was added to 7.6 g (0.028 mole) of mercuric chloride contained in a 50-ml flask fitted with a reflux condenser. An exothermic reaction, leading to reflux of ether, was found to take place. After the reaction subsided, the mixture was heated over a 1-h period, and then solvent ether was completely evaporated in vacuum.

Then, 35 ml of ethanol was added to the residue. The mixture was warmed for 30 min. The precipitate was filtered off and washed with two 60-ml portions of ethanol. To the filtrate was added 50 ml of water and this was allowed to stand overnight to give 6.5 g (62 % yield) of needle-like crystals, of pentamethyldisilanylmethylmercuric chloride, m.p. 69–70° (after recrystallization from 70 % aqueous ethanol). It was analyzed for mercury by the titration method of Whitmore and Sabatzki[18]. (Found: Hg, 53.05. $C_6H_{17}ClHgSi_2$ calcd.: Hg, 52.18 %.)

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SUMMARY

An investigation has been made of the synthesis of two new organofunctional disilanes, (dichloromethyl)pentamethyldisilane and 1,2-bis(chloromethyl)tetramethyldisilane, and some reactions of these and the previously reported (chloromethyl)pentamethyldisilane. (Dichloromethyl)pentamethyldisilane undergoes intramolecular rearrangement with anhydrous aluminum chloride to give either (trimethylsilyl)(chlorodimethylsilyl)chloromethane or 1,1-bis(chlorodimethylsilyl)ethane according to the reaction conditions. (Chloromethyl)pentamethyldisilane rearranges intramolecularly with sodium ethoxide in ethanol to give (trimethylsilyl)(ethoxydimethylsilyl)methane. Some other reactions known to occur with the chloromethyl derivatives of monosilane have also been studied.

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