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Synthesis and Intramolecular Rearrangements of Chloromethylpentamethyldisilane and 1-Chloromethyl-2-chlorotetramethyldisilane

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Chloromethylpentamethyldisilane (I) was prepared by two methods: (*1*) photochemical chlorination of the disilane fraction, followed by methylation with Grignard reagent and (*2*) peroxide-catalyzed chlorination of hexamethyldisilane. 1-Chloromethyl-2-chlorotetramethyldisilane (II) was prepared by demethylation of I with concentrated sulfuric acid, followed by treatment with ammonium chloride. Intramolecular rearrangements of I and II with anhydrous aluminum chloride led to the formation of the corresponding disilmethylene derivatives, indicating that the substituted silyl groups migrate in preference to a methyl group.

The literature of organosilicon compounds contains no example of a disilane with an aliphatic organo-functional substituent. In the present paper there is presented the synthesis of the first two compounds of this type having both a silicon-silicon linkage and a chloromethyl group in the molecule, and there is described an interesting observation on their intramolecular rearrangements with aluminum chloride.

The preparation of a chloromethyldisilane was first accomplished through peroxide-catalyzed chlorination with sulfuryl chloride of hexamethyldisilane. However, extensive cleavage of the silicon-silicon bond took place,[1] and the yield of the desired chloromethyldisilane (I) was only 42%.

$$Me_3SiSiMe_3 \xrightarrow[(PhCO_2)_2]{SO_2Cl_2} Me_3SiCl + Me_3SiSiMe_2CH_2Cl$$

I

A more satisfactory method for introducing a chloromethyl group into the disilane was the liquid phase photochemical chlorination of the disilane fraction of the methylchlorosilane residue,[2] followed by methylation with Grignard reagent, as indicated by the following sequence

$$Me_n\,Cl_{6-n}\,Si_2 \xrightarrow[U.V.]{Cl_2} ClCH_2Me_{n-1}Cl_{6-n}Si_2 \xrightarrow{MeMgBr}$$

disilane fraction

$$ClCH_2Me_2SiSiMe_3$$

I

In marked contrast to hexamethyldisilane and methylchlorodisilanes of lower chlorine content, the disilane fraction was found so stable to silicon-silicon cleavage that photochemical chlorination was carried out as successfully as that of methylchlorosilanes.[3] Fractional distillation at reduced pressure of the chlorination product gave no definite compound but a fraction consisting of a rather complex mixture of monochloromethyl derivatives of disilanes and probably of siloxanes as well. Exhaustive methylation of the fraction followed by treatment with concentrated sulfuric acid in the cold, for the purpose of removing siloxanes, rendered fractionation easy, yielding a pure sample of chloromethylpentamethyldisilane (I).

The second chloromethyl-containing disilane, 1-chloromethyl-2-chlorotetramethyldisilane (II) was prepared from compound I by applying to it an excellent technique of Sommer and his coworkers[4] which involves the reaction with concentrated sulfuric acid of trimethylsilyl containing compounds under proper conditions to give selective cleavage of one methyl group from a trimethylsilyl group. The demethylation of I took place very smoothly at about 40° to give nearly 90% of the theoretical yield of methane in a period of a few hours and to leave a homogeneous sulfuric acid solution. Addition of ammonium chloride to the solution yielded an organic layer, which on fractionation gave highly pure compound II in average yield of 70%.

$$I \xrightarrow[2.\ NH_4Cl]{1.\ H_2SO_4} ClCH_2Me_2SiSiMe_2Cl + CH_4$$

II

Structure proof for II was afforded by cleaving the ethylated product (III) with bromine in ethyl bromide.[5] Dimethylethylbromosilane was isolated as a cleavage fragment in almost theoretical yield, while another fragment of cleavage was recovered in part as bromomethyldimethylbromosilane. Not all of the chloromethyl-containing moiety was

(1) *Cf.* M. Kumada, K. Shiina, and M. Yamaguchi, *J. Chem. Soc., Japan, Ind. Chem. Sect.*, **57**, 230 (1954) [*Chem. Abstr.*, **49**, 11542 (1955)].

(2) The disilane fraction refers to a fraction boiling over the range 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 $MeCl_2SiSiMeCl_2$ and $Me_2ClSiSiMeCl_2$, somewhat contaminated by siloxanes. See M. Kumada, M. Yamaguchi, Y. Yamamoto, J. Nakajima, and K. Shiina, *J. Org. Chem.*, **21**, 1264 (1956).

(3) J. L. Speier, *J. Am. Chem. Soc.*, **73**, 824 (1951).

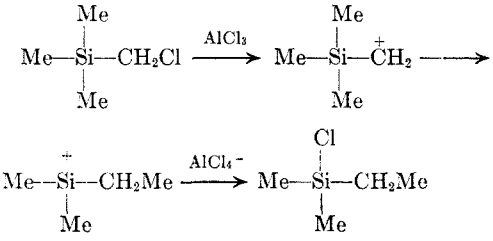
(4) L. H. Sommer, N. S. Marans, G. M. Goldberg, J. Rockett, and R. P. Pioch, *J. Am. Chem. Soc.*, **73**, 882 (1951) and subsequent papers.

(5) See ref. 1, and H. Gilman, R. K. Ingham, and A. G. Smith, *J. Org. Chem.*, **18**, 1743 (1953), for cleavage of alkyl-substituted disilanes by bromine.

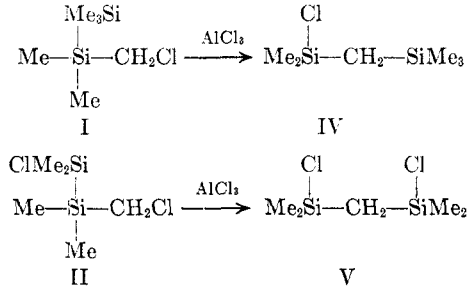
accounted for in the latter product, some having been lost in the intermediate fraction probably containing chloromethyldimethylbromosilane.

$$\text{II} \xrightarrow{\text{EtMgBr}} \underset{\text{III}}{\text{ClCH}_2\text{Me}_2\text{SiSiMe}_2\text{Et}} \xrightarrow{\text{Br}_2} \text{Me}_2\text{EtSiBr} + \text{BrCH}_2\text{Me}_2\text{SiBr}$$

Whitmore and his collaborators[6,7] have reported intramolecular rearrangements of chloromethyl and chloroethyl derivatives of silicon with anhydrous aluminum chloride. Thus, in case of chloromethyltrimethylsilane a methyl group migrates with its shared electron pair from silicon to the electron-deficient carbon, as formulated below:



It was of considerable interest to us to determine which group, methyl or the substituted silyl, should migrate more easily if the rearrangement be carried out with compounds I and II. A very clear-cut result was obtained in each case. Pentamethylchlorodisilmethylene (IV) was the only product isolated from I, while tetramethyl-1,3-dichlorodisilmethylene (V) was the only product from II, thus indicating that both silyl groups, Me_3Si and Me_2ClSi, have much greater migratory aptitudes than the methyl group. Regardless of the detailed mechanism,[8] the reactions are formulated as follows:



Evidence that the reaction represented by the former of the above two equations produced compound IV, not isomeric $Me_3SiSiClMeEt$, was afforded by the following facts. First, the product was quite indifferent to the action of bromine, indicating the absence of a Si—Si bond.[9] Second, the Raman spectrum[10] was practically identical with that of an authentic sample prepared by treating dimethyldichlorosilane with trimethylsilylmethylmagnesium chloride. Other physical properties of the two samples also conformed. The structure V was demonstrated by its insusceptibility to the attack of bromine,[9] by comparison of the physical properties with those reported for this compound in the literature,[11,12] and by its conversion, on hydrolysis, to the known dihydroxy derivative,[11,13] $HOMe_2SiCH_2SiMe_2OH$, and its cyclic dimeric dehydration product,[11,13] $(Me_2SiCH_2SiMe_2O-)_2$. Further studies of the chemical properties of compounds I and II are in progress.

EXPERIMENTAL[14]

Starting materials. The higher-boiling residue of methylchlorosilanes was supplied by the Tokyo-Shibaura Elec. Co., Ltd. The disilane fraction, b.p. *ca.* 150–160°, was obtained by fractionation of the residue through a 1.3 × 100 cm. Fenske column.

Chloromethylpentamethyldisilane (I). The chlorination technique followed in detail that used by Speier[3] in the chlorination of methylchlorosilanes. For example, from the chlorination of 1061 g. of the disilane fraction (% Cl, 56.2) in the presence of light from an incandescent lamp at 50–60°, 1202 g. of a product boiling over the range 70–185° at 50 mm. was obtained upon flash distillation at reduced pressure. Redistillation through a 1.3 × 100 cm. Fenske column gave the following fractions: (*a*) recovered disilane fraction, b.p. 45–55° (13 mm.), 543 g.; (*b*) mainly, monochloromethyl disilanes, b.p. 80–100° (17 mm.), 409 g.; and (*c*) polychlorination products, b.p. 100–145° (17 mm.), 133 g.

To the Grignard reagent prepared from 74 g. (3.05 g.-atoms) of magnesium and 300 g. (3.17 moles) of methyl bromide in 1.5 l. of absolute ether was differentially added 170 g. of fraction (*b*) (titrable Cl, 51.6%) with stirring and external cooling. After completion of addition the reaction mixture was heated to reflux for 9 hr. A large part of the ether was distilled off and then the mixture was hydrolyzed with dilute hydrochloric acid. The organic layer was separated, washed until neutral, and dried over calcium chloride, and then solvent ether was distilled.

An additional run, identical to the above, was carried out.

(6) F. C. Whitmore, L. H. Sommer, and J. R. Gould, *J. Am. Chem. Soc.*, **69**, 1976 (1947).

(7) L. H. Sommer, D. L. Bailey, J. R. Gould, and F. C. Whitmore, *J. Am. Chem. Soc.*, **76**, 801 (1954).

(8) The sum of the bond energies of the linkages of Si—Si and C—C is 135.9 kcal./mole. The corresponding value for 2Si—C is 150.0 kcal./mole [*cf.* H. Gilman and G. E. Dunn, *Chem. Revs.*, **52**, 77 (1953)]. Thus, the thermodynamic stability of $ClMe_2SiCH_2SiMe_3$ and $ClMe_2SiCH_2SiMe_2Cl$ exceeds that of $Me_3SiSiClMeEt$ and $ClMe_2SiSiClMeEt$, respectively, by 14.1 kcal./mole.

(9) Unpublished results in this laboratory indicate that methylchlorodisilanes of lower chlorine content such as $Me_3SiSiMe_2Cl$ and $Me_2ClSiSiMe_2Cl$ react vigorously with bromine in the cold to give Si—Si fission products; hence, it would not be unreasonable to expect that the disilanes such as $Me_3SiSiClMeEt$ and $Me_2ClSiSiClMeEt$ will also react with bromine.

(10) The authors are indebted to Dr. H. Murata of Osaka Municipal Technical Research Institute for Raman data.

(11) B. A. Bluestein, *J. Am. Chem. Soc.*, **70**, 3068 (1948).

(12) R. O. Sauer and E. M. Hadsell, *J. Am. Chem. Soc.*, **70**, 3590 (1948).

(13) M. Kumada and A. Habuchi, *J. Inst. Polytech., Osaka City Univ., Ser. C*, **3**, 65 (1952) [*Chem. Abstr.*, **48**, 9907 (1954)].

(14) All temperatures reported here are uncorrected. Molar refractions were calculated by the method of Vogel *et al.* [A. I. Vogel, W. T. Cresswell, and J. Leicester, *J. Phys. Chem.*, **58**, 174 (1954)]. Silicon analyses were made by a method previously reported (ref. 2).

Crude products from the two runs were combined and treated with sulfuric acid in the cold leaving an acid-insoluble colorless layer, which was, after washing with dilute sodium bicarbonate, fractionally distilled under vacuum in a modified Stedman column rated at about 20 theoretical plates to give chloromethylpentamethyldisilane, b.p. 87.0–87.5° at 58 mm., m.p. 6–7°, n_D^{20} 1.4576, d_4^{20} 0.8837, MR 55.77 (calcd. 56.03), in addition to 17 g. of forerun and 56 g. of after-run, b.p. 107–110° (58 mm.).

Anal. Calcd. for $C_6H_{17}ClSi_2$: Si, 31.1. Found: Si, 30.9, 31.0.

Peroxide-catalyzed chlorination of hexamethyldisilane. In a 100-ml. three-necked flask equipped with an air-tight stirrer, a dropping funnel, and an efficient reflux condenser leading to a Dry Ice–acetone trap there was placed 40 g. (0.27 mole) of hexamethyldisilane. All exits were protected by calcium chloride drying tubes. Sulfuryl chloride (36.5 g., 0.27 mole) containing 0.2 g. of benzoyl peroxide was added dropwise with stirring over 3 hr. at a temperature of 80–90°. Then the mixture was heated to reflux. The reaction was assumed to be complete when further heating caused no increase in liquid (sulfur dioxide) in the trap. The content of the reaction flask was then fractionally distilled in a small Stedman column (initially, at atmospheric pressure; later, at reduced pressure) to give the following two fractions: (*a*) trimethylchlorosilane, b.p. 57.0–58.5°, n_D^{20} 1.3850 (literature,[15] b.p. 57.7°; literature,[16] b.p. 58° (734 mm.), n_D^{20} 1.3884), % Cl 31.9 (calcd. 32.7), 25 g., yield 43%; and (*b*) chloromethylpentamethyldisilane, b.p. 60° at 14 mm., n_D^{20} 1.4578, d_4^{20} 0.8835, 22 g., yield 42%.

1-Chloromethyl-2-chlorotetramethyldisilane (II). This compound was prepared from I in essentially the same manner as that previously reported for methyldisilanes with chlorine attached to silicon.[2] A 500-ml. three-necked flask was fitted with an air-tight stirrer, a thermometer, and a gas-outlet tube which was connected to an apparatus for collecting gas. In the flask were placed 50 g. (0.25 mole) of compound I and 200 g. of concd. sulfuric acid of sp. gr. 1.84. The mixture was stirred at 38 ± 2°. The reaction began at once as evidenced by the evolution of gas. After 2 hr. 6.0 l. (91%) of methane was collected and no more gas evolved on further stirring. At this point the mixture was cooled by means of an ice bath and 30 g. (0.56 mole) of dry pulverized ammonium chloride was added to the mixture with stirring. Stirring was continued for an additional 30 min. Separation followed by fractionation through a Stedman column of 20 theoretical plates gave practically a single substance, 1-chloromethyl-2-chlorotetramethyldisilane, b.p. 79.5° at 17 mm., m.p. *ca.* 9°, n_D^{20} 1.4735, d_4^{20} 1.0206, MR 55.45 (calcd. 55.59), 38 g., yield 70%.

Anal. Calcd. for $C_5H_{14}Cl_2Si_2$: Cl (titrable), 17.6. Found: Cl (titrable), 17.7.

1-Chloromethyl-2-ethyltetramethyldisilane (III). Compound II, 46 g. (0.22 mole), was added to a Grignard solution prepared from 6.5 g. (0.27 g.-atom) of magnesium and 30 g. (0.28 mole) of ethyl bromide in 100 ml. of ether. Heating to reflux for 8 hr. produced a white granular precipitate. The reaction mixture was then hydrolyzed with dilute hydrochloric acid. Separation, washing, and drying of the organic layer was followed by distillation of the solvent, which left 42 g. of a residue. It was then treated with concd. sulfuric acid in the cold, yielding 37 g. of an acid-insoluble layer. Rectification of this layer furnished 30 g. (68%) of 1-chloromethyl-2-ethyltetramethyldisilane, b.p. 79° at 26 mm., n_D^{20} 1.4662, d_4^{20} 0.8933, MR 60.85 (calcd. 60.68).

Anal. Calcd. for $C_7H_{19}ClSi_2$: Si, 28.8. Found: Si, 28.8.

Cleavage of compound III *with bromine.* To a stirred solution of 19 g. (0.098 mole) of III in 30 g. of ethyl bromide was gradually added a solution of 16 g. (0.1 mole) of bromine in 30 g. of ethyl bromide at room temperature. Initially, instantaneous decolorization took place with considerable evolution of heat, but later, it was necessary to heat the mixture to reflux. After complete addition of the bromine, the mixture was refluxed for an additional 3 hr. to insure completeness of reaction. Then it was submitted to fractional distillation to give the following fractions: (*a*) dimethylethylbromosilane, b.p. 110–110.5° (calcd. b.p.[17] 110.4°), 15.8 g. (99%), % Br 50.0 (calcd. 48.4); (*b*) intermediate fraction, b.p. 130–140° (mostly at 133°), 7.5 g.; and (*c*) bromomethyldimethylbromosilane, b.p. 154°, 7.3 g. (32%), % Br (titrable) 36.0 (calcd. 34.4).

Intermolecular rearrangement of compound I. To 40 g. (0.22 mole) of compound I stirred and protected from moisture was added a small amount of anhydrous aluminum chloride. A vigorous, exothermic reaction took place and it was necessary to cool the flask. When the reaction subsided gentle heat was applied to the flask for a short period of time and then an additional small amount of aluminum chloride was introduced with cooling. Addition of catalyst with cooling and application of heat to the flask was continued repeatedly until no more noticeable change occurred. During the period (*ca.* 10 hr.) required to complete the reaction it was necessary to add a total of *ca.* 1 g. of catalyst. The reaction mixture was heated on a steam bath for an additional 3 hr., and then was flash-distilled under vacuum to separate the product from aluminum catalyst. Fractionation of this catalyst-free distillate (37 g.) through a Stedman column gave 32 g. (82%) of pentamethylchlorodisilmethylene, b.p. 153°, n_D^{20} 1.4322, d_4^{20} 0.8846 (literature,[18] b.p. 154.5° (740 mm.), n_D^{25} 1.4277, d^{25} 0.8662; literature,[19] b.p. 154–5°, n_D^{20} 1.4320, d_4^{20} 0.8846), MR 53.03 (calcd. for $Me_3SiCH_2SiMe_2Cl$ 53.24; calcd. for $Me_3SiSiMeEtCl$ 55.39), % Cl 19.6 (calcd. 19.6). A sample of this compound did not react with bromine at all even on heating, indicating complete absence of silicon-silicon linkage in the molecule. This compound was further characterized by comparison of its Raman spectrum with that of an unequivocal sample (b.p. 153°, n_D^{20} 1.4310) prepared from trimethylsilylmethylmagnesium chloride and dimethyldichlorosilane (Table I).

TABLE I

COMPARISON OF RAMAN SPECTRA FOR SAMPLES OF PENTAMETHYLCHLORODISILMETHYLENE FROM TWO DIFFERENT SOURCES

Rearrangement Product		Grignard Product	
$\Delta\nu$[a]	I[b]	$\Delta\nu$[a]	I[b]
165	(3s)	165	(6s)
193	(4s)	190	(6s)
229	(4s)	230	(5s)
260	(2s)	257	(4s)
333	(2s)	332	(3s)
406	(4s)	409	(3s)
463	(4s)	465	(5s)
572	(7s)	570	(6s)
632	(3s)	635	(3s)
685	(5s)	685	(5s)
1258	(2s)	1255	(3s)
1322	(3s)	1325	(5s)
1408	(4b)	1405	(5b)
2824	(3b)	—	—
2900	(10s)	2897	(10s)
2972	(10s)	2970	(10s)

[a] $\Delta\nu$ = Raman displacement in cm.$^{-1}$ [b] I = relative intensity; s = sharp; b = broad.

(15) W. F. Giliam and R. O. Sauer, *J. Am. Chem. Soc.*, **66**, 1793 (1944).

(16) B. O. Pray, L. H. Sommer, G. M. Goldberg, G. T. Kerr, P. A. Digiorgio, and F. C. Whitmore, *J. Am. Chem. Soc.*, **70**, 433 (1948).

(17) R. N. Lewis and A. E. Newkirk, *J. Am. Chem. Soc.*, **69**, 701 (1947).

(18) J. T. Goodwin, U. S. Patent **2,507,518** [*Chem. Abstr.*, **45**, 3410 (1951)].

(19) I. Hizawa and E. Nojimoto, *J. Chem. Soc., Japan, Ind. Chem. Sect.*, **59**, 1359 (1956).

Intramolecular rearrangement of compound II. The procedure was the same as above except that 50 g. (0.25 mole) of compound II was allowed to react with a total of 1.8 g. of aluminum chloride. Fractionation of the catalyst-free distillate (41 g.) through a column similar to that used above gave 25 g. (50%) of tetramethyl-1,3-dichlorodisilmethylene, b.p. 58° at 10 mm., n_D^{20} 1.4483, d_4^{20} 1.013, MR 53.22 (calcd. for $Me_2ClSiCH_2SiMe_2Cl$ 52.78; calcd. for $Me_2ClSiSiMeEtCl$ 56.83), % Cl 35.6 (calcd. 35.6). This substance did not react with bromine even on heating, indicating no presence of silicon-silicon bond in the molecule. A boiling point of 95° at 50 mm., n_D^{20} 1.4480, d_4^{20} 1.016 has been reported[11] for tetramethyl-1,3-dichlorodisilmethylene.

Another fraction, a total of 9.0 g., b.p. 60–64° (10 mm.), n_D^{20} 1.4675–1.4711, was obtained. This fraction reacted vigorously both with bromine and with aluminum chloride in the cold; hence, it undoubtedly seemed to be a mixture containing the unchanged starting material.

Hydrolysis of tetramethyl-1,3-dichlorodisilmethylene. In accordance with the procedure (Method A) by George, Sommer, and Whitmore[20] for dialkylsilanediols from dialkyldichlorosilanes, to a vigorously stirred mixture of 100 ml. of aqueous solution of sodium hydroxide (5 g.) and 50 ml. of ether was added a solution of 10 g. (0.05 mole) of tetramethyl-1,3-dichloro-disilmethylene in 100 ml. of ether over a period of 4 min. at 0°. The ether solution combined with a single ether extract of the aqueous layer was worked up in essentially the same manner as that of the literature,[20] giving 4.4 g. of white needles melting at 86.5–87.0° (literature,[11] m.p. 84–86°; literature,[13] m.p. 86.5°) when petroleum ether (b.p. 45–60°) was added. Concentration of the mother liquor gave an additional 1.2 g. of white needles, m.p. 86.5°. The two crops constituted a 68% yield of tetramethyldisilmethylene-1,3-diol. Complete removal of the solvent from the mother liquor by evaporation left 2 g. of oily matter which mostly solidified at 0°. A week later, a large rhombic plate of 2,2,4,4,6,6,8,8-octamethyl-1,5-dioxa-2,4,6,8-tetrasilacyclooctane, m.p. 27° (literature[11–13] 28–29°), 0.21 g., crystallized from the oil.

(20) P. D. George, L. H. Sommer and F. C. Whitmore, *J. Am. Chem. Soc.*, **75**, 1585 (1953).

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