REACTIONS OF (CHLOROMETHYL)PENTAMETHYLDISILANE WITH SOME NUCLEOPHILIC REAGENTS

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INTRODUCTION

In a previous communication from this laboratory[1], it was shown that (chloromethyl)pentamethyldisilane $ClCH_2(CH_3)_2SiSi(CH_3)_3$ (I) selectively undergoes three different types of nucleophilic reactions, depending upon the nature of the reagent used. Thus, by iodide ion in acetone, substitution of the chlorine atom took place to give (iodomethyl)pentamethyldisilane; ethoxide ion in ethanol caused intramolecular rearrangement to give ethoxypentamethyldisilylmethane; while cyanide ion in ethanol gave cleavage of the silicon–carbon bond to yield ethoxypentamethyldisilane. Continuing this work we have now studied the reactions of compound (I) with further several nucleophilic reagents. Moreover, in connection with carbon-functional organo-disilanes, certain compounds that could not be obtained by the nucleophilic substitution have been prepared through alternative routes.

RESULTS AND DISCUSSION

As nucleophilic reagents, we selected the following systems: $CH_3ONa–CH_3OH$, iso-C_3H_7ONa–iso-C_3H_7OH, tert-C_4H_9ONa–tert-C_4H_9OH, C_6H_5ONa–C_6H_5OH, C_2H_5SNa–C_2H_5SH, C_6H_5SNa–C_6H_5SH, $(C_2H_5)_2NH$, $C_6H_5NH_2$, and CH_3CO_2K–CH_3CO_2H. The reaction mixture was heated either in a sealed glass tube or in a flask at an ordinary pressure for a given period of time. Sometimes, the reaction was followed by gas chromatography. Structure proof for the reaction products was based on their infrared spectra as well as their behavior towards bromine. As has been reported recently by Fritz et al.[2], the infrared spectra of compounds with $SiCH_2Si$ structure exhibit a band near 1050 cm^{-1} assignable to the deformation vibration of the C–H bond of this group, while those of $SiSiCH_2$ compounds do not. Compounds containing the silicon–silicon bond react with bromine violently in the cold, whereas compounds with the $SiCH_2Si$ structure, in general, do not. Of course, this test is invalid, if the compound contains any group (for instance, NHC_6H_5) as sensitive as the silicon–silicon bond to the action of bromine.

As was observed previously[1] with C_2H_5ONa–C_2H_5OH, only rearrangement products, $(CH_3)_3SiCH_2Si(CH_3)_2OR$ (II, R = CH$_3$; III, R = iso-C_3H_7; IV, R = C_6H_5), were obtained when methoxide, isopropoxide and phenoxide reagents were used. In the case of tert-butoxide, the starting substance (I) was recovered unchanged even on heating in a sealed tube at 150° for 125 h. Doubtless, this is because of steric hindrance.

With the mercaptides and the amines, only substitution products $(CH_3)_2SiSi-$

$(CH_3)_2CH_2Y$ (V, $Y = SC_2H_5$; VI, $Y = SC_6H_5$; VII, $Y = N(C_2H_5)_2$; VIII, $Y = NHC_6H_5$) were obtained as in the reaction with iodide ion, previously reported[1].

The reaction with acetate ion in acetic acid was found to proceed in two steps: first, substitution leading to the formation of (acetoxymethyl)pentamethyldisilane (IX); second, intramolecular rearrangement to give acetoxypentamethyldisilyl-methane (X). Following the reaction by gas chromatography revealed that the substitution product appeared about 1 h after heating was started, some amount of the rearrangement product was formed about 20 h later and the rearrangement was complete at the point of 117 h. In order to confirm the thermal intramolecular rearrangement of (acetoxymethyl)pentamethyldisilane, we prepared it by the reaction of (hydroxymethyl)pentamethyldisilane[3] with acetic anhydride.

$$(CH_3)_3SiSi(CH_3)_2CH_2OH + (CH_3CO)_2O \longrightarrow (CH_3)_3SiSi(CH_3)_2CH_2OOCCH_3 + CH_3COOH$$
$$(IX)$$
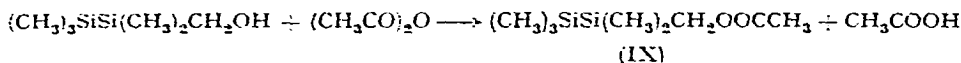
Indeed, (acetoxymethyl)pentamethyldisilane (IX) was converted, under reflux conditions, into acetoxypentamethyldisilylmethane (X) in 6.5 h in bulk, but after several tens of hours in an acetic acid solution. It seems likely that the intramolecular rearrangement of compound (IX) will proceed via a cyclic transition state as shown below:

(IX)   (X)
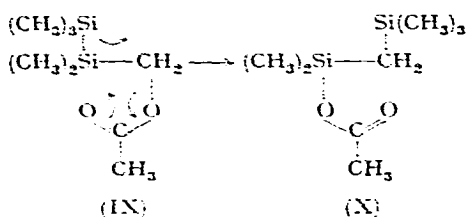
All attempts to prepare (methoxymethyl)pentamethyldisilane (XI) from $(CH_3)_3SiSi(CH_3)_2CH_2X$ (X = Cl, I) compounds failed. Thus, the reaction of (chloromethyl)pentamethyldisilane (I) with sodium methoxide in n-heptane as well as in ethylene glycol dimethyl ether resulted only in the formation of the methoxypentamethyldisilylmethane (II). Treatment of (iodomethyl)pentamethyldisilane[1] with silver oxide in methanol also gave a rearrangement product, $[(CH_3)_3SiCH_2Si(CH_3)_2]_2O^*$. The successful preparation of the desired compound, however, was attained by the reaction of chloropentamethyldisilane with monochloromethyl ether in the presence of magnesium in tetrahydrofuran (THF), which is an application of the method recently disclosed in the patent literature[1].

$$(CH_3)_3SiSi(CH_3)_2Cl + ClCH_2OCH_3 \xrightarrow[THF]{Mg} (CH_3)_3SiSi(CH_3)_2CH_2CCH_3 \quad (XI)$$
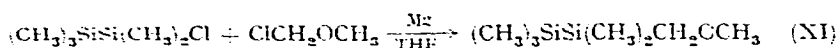
It is noteworthy that the (methoxymethyl)pentamethyldisilane (XI), once prepared, was surprisingly stable to the action of methoxide and ethoxide ion. No change was detected by gas-chromatographic analysis when the reaction mixture was subjected to conditions under which the formation of the alkoxypentamethyl-

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* When we were adding silver perchlorate in portions to a stirred mixture of (hydroxymethyl)pentamethyldisilane and methyl iodide in the cold, the temperature of the reaction mixture rose suddenly, and a violent explosion occurred.

disilylmethane from the reaction of (chloromethyl)pentamethyldisilane (I) with the alkoxide ion would be complete.

(Cyanomethyl)pentamethyldisilane (XII) was successfully prepared through the reaction of pentamethyldisilanylmethylmagnesium chloride with cyanogen, after the technique used by Prober[5] for the preparation of the corresponding monosilane compound.

$$(CH_3)_3SiSi(CH_3)_2CH_2MgCl + (CN)_2 \longrightarrow (CH_3)_3SiSi(CH_3)_2CH_2CN \quad (XII)$$
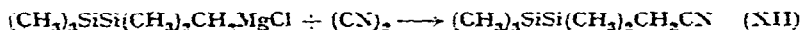
It was found that this compound was stable when refluxed in a pure ethanol solution, but underwent complete cleavage of the cyanomethyl group to give ethoxypenta-methyldisilane when refluxed in ethanol containing a catalytic amount of cyanide ion.

$$(CH_3)_3SiSi(CH_3)_2CH_2CN + C_2H_5OH \xrightarrow{CN^-} (CH_3)_3SiSi(CH_3)_2OC_2H_5 + CH_3CN$$
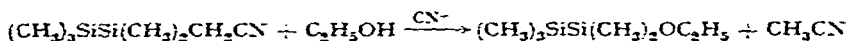
From these observations it seems likely that the differences in thermodynamic stability between the rearrangement and substitution products formed in a given nucleophilic reaction of (chloromethyl)pentamethyldisilane (I) may be a major factor in determining the direction of the reaction. Thus, the relatively large difference in calculated bond energies (see e.g. ref. 6) between the structures SiCH$_2$SiOR and SiSiCH$_2$OR (49.1 kcal/mole) favors the formation of the rearrangement product, while only substitution products are formed in cases of iodide ion, mercaptide ions and amines because the corresponding bond energy differences are not very large: SiCH$_2$SiI — SiSiCH$_2$I 27.0, SiCH$_2$SiSR — SiSiCH$_2$SR 34.0, SiCH$_2$SiNR$_2$ — SiSi-CH$_2$NR$_2$ 28.2 and SiCH$_2$SiCN — SiSiCH$_2$CN 14.1 kcal/mole. Doubtless, easy cleavage of the cyanomethyl group from silicon in the presence of an anion is due to high electronegative nature of the CH$_2$CN group. A satisfactory explanation of the observed high stability of (CH$_3$)$_3$SiSi(CH$_3$)$_2$CH$_2$OCH$_3$, once formed, to intramolecular rearrange-ment, of course, is not given by the simple considerations on the basis of bond energy calculation, but requires further information from the mechanistic investigation, which will be the future subject of our program.

Formulas and some physical properties of the compounds prepared in the present study are listed in Table 1, and molar refractions and analytical data in Table 2.

TABLE 1

PHYSICAL PROPERTIES OF REACTION PRODUCTS FROM (CHLOROMETHYL)PENTAMETHYLDISILANE (I)

No.	Formula	B.p. (°C/mm)	n_D^{20}	d_4^{20}
(II)	(CH$_3$)$_3$SiCH$_2$Si(CH$_3$)$_2$OCH$_3$[a]	58/32	1.4170	0.8154
(III)	(CH$_3$)$_3$SiCH$_2$Si(CH$_3$)$_2$O-iso-C$_3$H$_7$	ca. 88/56	1.4190	0.8118
(IV)	(CH$_3$)$_3$SiCH$_2$Si(CH$_3$)$_2$OC$_6$H$_5$	86/3.5	1.4821	0.9134
(V)	(CH$_3$)$_3$SiSi(CH$_3$)$_2$CH$_2$SC$_2$H$_5$	94/13	1.4778	0.8523
(VI)	(CH$_3$)$_3$SiSi(CH$_3$)$_2$CH$_2$SC$_6$H$_5$	109/2	1.5419	0.9485
(VII)	(CH$_3$)$_3$SiSi(CH$_3$)$_2$CH$_2$N(C$_2$H$_5$)$_2$	82/15	1.4549	0.7986
(VIII)	(CH$_3$)$_3$SiSi(CH$_3$)$_2$CH$_2$NHC$_6$H$_5$	104/1.5	1.5247	0.9070
(IX)	(CH$_3$)$_3$SiSi(CH$_3$)$_2$CH$_2$OOCCH$_3$	72/14	1.4424	0.8774
(X)	(CH$_3$)$_3$SiCH$_2$Si(CH$_3$)$_2$OOCCH$_3$	80/21	1.4240	0.8837
(XI)	(CH$_3$)$_3$SiSi(CH$_3$)$_3$CH$_2$OCH$_3$	57/37	1.4342	0.7982
(XII)	(CH$_3$)$_3$SiSi(CH$_3$)$_2$CH$_2$CN	105/25[b]		

[a] Lit.[7] b.p. 148–152°, n_D^{25} 1.4120, d_4^{25} 0.813. [b] M.p. ca. 30°.

TABLE 2

MOLAR REFRACTIONS AND ANALYTICAL DATA

No.	MR_D		C %		H %	
	Found	Calcd.[a]	Found	Calcd.	Found	Calcd.
(II)	54.40	54.50	47.98	47.66	11.61	11.43
(III)	63.62	63.80	52.92	52.87	11.71	11.83
(IV)	74.45	74.55	60.18	60.43	9.38	9.30
(V)	68.56	68.40	46.25	46.53	10.46	10.74
(VI)	84.46	83.50	56.76	56.62	8.63	8.71
(VII)	73.88	73.56	55.09	55.22	12.50	12.51
(VIII)[b]	80.07	79.18	61.19	60.69	9.98	9.76
(IX)	61.69	62.07	47.27	47.00	9.63	9.86
(X)	59.09	59.04	47.43	47.00	10.27	9.86
(XI)	57.58	57.61	47.56	47.66	11.14	11.43
(XII)[c]	—	—	49.32	49.06	10.08	10.00

[a] See ref. 8. [b] N % found 5.89. calcd. 5.90. [c] N % found 8.60. calcd. 8.17.

EXPERIMENTAL

All temperatures reported here are uncorrected. (Chloromethyl)pentamethyl-disilane (I) was prepared as reported previously[1].

Reactions of compound (I)

(1) *With CH_3ONa in CH_3OH.* Sodium (2.1 g, 0.091 g-atom) was dissolved in 30 ml of absolute methanol in a 2.6 × 50 cm glass tube. To the solution was added 15 g (0.083 mole) of (I). The tube was flushed with nitrogen, sealed, and heated in an oil bath at 95–110° for 15 h. Ether was then used to transfer the contents of the opened tube to a flask, and the mixture neutralized cautiously by passing dry hydrogen chloride. The precipitate was filtered and washed with ether. The filtrate was combined with washings and fractionally distilled in a small column rated at about 20 theoretical plates to give 5.7 g (40 % yield) of gas–chromatographically homogeneous methoxy-pentamethyldisilylmethane (II). Gas-chromatographic analysis of the distillation residue showed the presence of $[(CH_3)_3SiCH_2Si(CH_3)_2]_2O$. Neither the distillate nor residue reacted with bromine. The IR spectrum of (II) showed significant bands at 1050 (C–H deformation in SiCH₂Si), 1094 (Si–O stretching) and 2830 cm⁻¹ (C–H stretching in OCH₃).

(2) *With CH_3ONa in $CH_3OCH_2CH_2OCH_3$.* To a dispersion of methanol-free sodium methoxide (0.06 mole) in ethyleneglycol dimethyl ether (30 ml) was added 10 g (0.056 mole) of (I) at room temperature with stirring. Reaction set in with considerable evolution of heat, which required cooling. Gas-chromatographic analysis showed that the reaction was complete after 30 min, and the only product was methoxypenta-methyldisilylmethane (II). Fractionation gave 6 g of (II).

(3) *With CH_3ONa in n-heptane.* This experiment was carried out in essentially the same manner as above except that 30 ml of n-heptane in place of ethyleneglycol dimethyl ether was used. It was necessary to continue stirring for 11 h to complete the reaction. Gas chromatography showed that the product was exclusively (II).

(4) *With iso-C_3H_7ONa in iso-C_3H_7OH.* In a similar glass tube to that used above, 10 g (0.056 mole) of (I) was allowed to react with 0.061 mole of sodium isopropoxide

in isopropyl alcohol at 95–110° for 22 h, and the reaction mixture was worked up as above. Fractional distillation gave 4 g of isopropoxypentamethyldisilylmethane (III) contaminated with about 30 % (by gas chromatography) of the starting material. Preparative gas chromatography gave a pure sample of (III) for analyses and measurements of physical properties. The product did not react with bromine. Its IR spectrum showed bands at 1050 (C–H deformation) and 1026 cm^{-1} (Si–O stretching).

(5) *With C_6H_5ONa*. Sodium phenoxide was prepared from 18 g (0.19 mole) of phenol and 5.2 g (0.13 mole) of sodium hydroxide dissolved in a small amount of water. To this mixture was added 500 ml of benzene; water was then removed completely together with benzene by distillation, initially at atmospheric pressure, later *in vacuo*. Compound (I) (20 g, 0.11 mole) was added to the residue and heated to reflux with stirring for 70 h. The precipitate was filtered off, and the filtrate was fractionally distilled to give 13 g (43 % yield) of phenoxypentamethyldisilylmethane (IV). It reacted with bromine as easily as phenol, but not as violently as any disilane derivative did. A small sample of the product was shaken with dilute hydrochloric acid, and a ferric chloride solution was added to it. The test for phenol was positive. The IR spectrum of (IV) showed bands at 1050 (C–H deformation) and 1030 cm^{-1} (Si–O stretching).

(6) *With C_2H_5SNa in C_2H_5SH*. A mixture of 15 g (0.083 mole) of (I) and sodium ethylmercaptide prepared from 2.1 g (0.091 g-atom) of sodium in 30 g (0.48 mole) of ethanethiol was heated in a 2.6 × 50 cm sealed glass tube at 95–110° over a period of 83 h. The contents of the reaction tube were filtered and flash-distilled. The salt-free distillate was redistilled in a column to give 13 g (76 % yield) of (ethylthiomethyl)-pentamethyldisilane (V). A sample of this compound did react violently with bromine in the cold. Its IR spectrum showed no band near 1050 cm^{-1}.

(7) *With C_6H_5SNa in C_6H_5SH*. A mixture of 15 g (0.083 mole) of (I) and 15 g of thiophenol containing 0.09 mole of sodium thiophenolate was heated in a similar tube to that above at 95–110° for 57 h and then at 130–150° for 45 h. Fractionation of the organic layer gave 13 g (62 %) of pure (phenylthiomethyl)pentamethyldisilane (VI). A sample of this compound did react with bromine violently. Its IR spectrum exhibited no band near 1050 cm^{-1}.

(8) *With $(C_2H_5)_2NH$*. In a sealed tube as above was heated a mixture of 15 g (0.083 mole) of (I) and 18.3 g (0.25 mole) of diethylamine at 95–110° for 54 h. At this point, we added 45 ml of 8 % aqueous solution of sodium hydroxide to the reaction mixture in order to dissolve the precipitated salt. The organic layer was separated and fractionally distilled to give 10.5 g (79 % yield on the basis of unrecovered (I)) of (diethylamino)methylpentamethyldisilane (VII). A sample of this compound violently reacted with bromine. Its IR spectrum showed no band near 1050 cm^{-1}.

(9) *With $C_6H_5NH_2$*. In a 100-ml flask, a mixture of 15 g (0.083 mole) of (I) and 24 g (0.25 mole) of aniline was heated with stirring at 100–130° for 21 h. To the mixture was then added 100 ml of 15 % aqueous solution of sodium hydroxide. Fractional distillation of the organic layer, separated and dried over calcium oxide, gave 7 g (36 % yield) of (anilinomethyl)pentamethyldisilane (VIII). The IR spectrum exhibited no band near 1050 cm^{-1} characteristic of the C–H deformation in the $SiCH_2Si$ group.

(10) *With tert-C_4H_9ONa in tert-C_4H_9OH (attempted)*. In a sealed tube a mixture of 15 g (0.083 mole) of compound (I), 0.91 mole of sodium tert-butoxide and 15 ml of

tert-butyl alcohol was heated at 95–110° over a period of 125 h. At this point all the starting substance (I) was recovered unchanged.

(*11*) *With CH_3CO_2K in CH_3CO_2H*. In a 100-ml flask we heated a mixture of 25 g (0.14 mole) of (I) and 17 g (0.17 mole) of fused potassium acetate in 25 ml of glacial acetic acid at 145° for 70 h. During the course of reaction, small samples were taken out from the mixture several times and analyzed gas-chromatographically. This analysis showed that a small amount of $(CH_3)_3SiSi(CH_3)_2CH_2O_2CCH_3$ (IX) appeared after 1 h, some quantity of $(CH_3)_3SiCH_2Si(CH_3)_2O_2CCH_3$ (X) had been formed after 20 h and the conversion to (X) was extensive after 70 h. Fractional distillation of the organic layer gave 14 g (50% yield) of acetoxypentamethyldisilylmethane (X), 4 g of a mixture of (IX) and (X), and 2 g of $[(CH_3)_3SiCH_2Si(CH_3)_2]_2O$, b.p. 126°/21 mm. A sample of (X) did not react with bromine. Its IR spectrum exhibited a fairly intensive, broad band near 1050 cm^{-1}, possibly attributable to the overlap of two bands of the C–H deformation in SiCH$_2$Si and the Si–O stretching vibration.

Preparation of (acetoxymethyl)pentamethyldisilane (IX)

A mixture of 5 g (0.03 mole) of (hydroxymethyl)pentamethyldisilane and 3.1 g (0.03 mole) of acetic anhydride was heated to reflux for 1 h. At this point the reaction was found to be complete by gas chromatography. Fractional distillation gave 4.5 g (71% yield) of (IX). A sample of this product did react with bromine violently. The IR spectrum showed no band near 1050 cm^{-1}, assignable to C–H deformation in SiCH$_2$Si structure.

Preparation and attempted reaction with sodium alkoxides, of (methoxymethyl)penta-methyldisilane (XI)

To a stirred mixture of 13.1 g (0.54 g-atom) of magnesium, a small quantity of mercuric chloride and 30 g (0.18 mole) of chloropentamethyldisilane in 300 ml of THF was added dropwise (2 h) 43.5 g (0.54 mole) of monochloromethyl ether diluted with 100 ml of THF with external cooling. The reaction mixture was allowed to stand overnight. It was then decomposed with a saturated solution of ammonium chloride. The organic layer was separated, dried over potassium carbonate and fractionally distilled to give 14 g (44% yield) of (methoxymethyl)pentamethyldisilane (XI). The IR spectrum of this compound exhibited a band at 1106 cm^{-1} characteristic of C–O stretching in ether structure, but no bands at 1050 (C–H deformation in SiCH$_2$Si) and at 1094 cm^{-1} (Si–O stretching). A sample of (XI) reacted with bromine violently. Another sample (0.5 ml) was heated to reflux in ethanol (2 ml) without undergoing any change for 8 h in the presence as well as absence of sodium ethoxide.

Reaction of (iodomethyl)pentamethyldisilane with silver oxide in methanol

To a stirred mixture of 12 g (0.044 mole) of (iodomethyl)pentamethyldisilane and 0.7 g (0.022 mole) of methanol was added 5.1 g (0.022 mole) of silver oxide in portions at room temperature. It was then heated at 60–70° for 3 h. Gas-chromatographic analysis of a sample from the reaction mixture indicated that the only product was $[(CH_3)_3SiCH_2Si(CH_3)_2]_2O$.

Preparation and cleavage of (cyanomethyl)pentamethyldisilane (XII)

To a stirred ether solution of 7.9 g (0.15 mole) of cyanogen was added dropwise

a Grignard solution, prepared from 30 g (0.17 mole) of (chloromethyl)pentamethyl-disilane (I), at —70°. The reaction mixture was allowed to stand overnight and then hydrolyzed with a saturated solution of ammonium chloride. The organic layer combined with several ether extracts was fractionally distilled to give 15 g (53% yield) of (cyanomethyl)pentamethyldisilane (XII). No band in its IR spectrum was shown near 1050 cm^{-1}. A sample of (XII) was refluxed in ethanol for 13 h without undergoing any change. Addition of a catalytic amount of sodium cyanide to the reaction system, however, gave rise to a complete cleavage of the cyanomethyl group from silicon within 3 h to produce ethoxypentamethyldisilane and acetonitrile (identified by gas chromatography).

SUMMARY

        (Chloromethyl)pentamethyldisilane (I) underwent intramolecular rearrangement when treated with sodium methoxide, isopropoxide and phenoxide to give the corresponding alkoxypentamethyldisilylmethanes $(CH_3)_3SiCH_2Si(CH_3)_2OR$, whereas it gave only substitution products of the formula $(CH_3)_3SiSi(CH_3)_2CH_2Y$ when allowed to react with sodium ethylmercaptide and thiophenolate, and with diethylamine and aniline. The reaction of (I) with potassium acetate in acetic acid proceeded in two steps: first, substitution; second, intramolecular rearrangement of the substitution product. Three organo-functional organodisilanes, viz. (acetoxymethyl)-, (methoxymethyl)- and (cyanomethyl)pentamethyldisilane, which could not be obtained by the nucleophilic substitution, were prepared by alternative methods and some of their reactions studied.

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