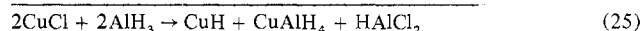
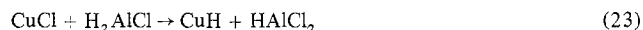
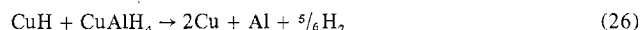


attempt was also made to study the reaction in THF; however, the reaction was found to be too slow at  $-40$  to  $-30^\circ$  and the reaction product decomposed above  $-20^\circ$ .

**Reactions of CuCl with  $\text{AlH}_3$ .** When cuprous chloride and  $\text{AlH}_3$  were allowed to react in 1:1 mole ratio in ether at  $-78^\circ$  and then allowed to warm slowly to room temperature, the reaction mixture turned completely black giving off a gas. The elemental analysis as well as an infrared spectrum of the filtrate suggests that the reaction takes place according to the sequence of eq 22–25.



The infrared spectrum of the filtrate showed a sharp band at  $1900\text{ cm}^{-1}$  with a shoulder at  $1850\text{ cm}^{-1}$ . Elemental analysis of the filtrate indicated only 43% of the total aluminum. The infrared spectrum of the black solid product did not show any absorption bands due to either hydridoaluminum compounds or hydridocopper compounds. Thus, it appears that the black solid product is a mixture of copper and aluminum metal formed according to eq 26. Since the filtrate was shown to be an ether solution of  $\text{HAlCl}_2$  and since half of the aluminum



was in the filtrate and half in the precipitate, it appears that there are ample data to suggest the above reaction sequence.

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**Registry No.**  $\text{AlH}_3$ , 7784-21-6;  $\text{AlH}_2\text{Cl}$ , 14644-71-4;  $\text{AlHCl}_2$ , 13497-97-7;  $\text{AlCl}_3$ , 7446-70-0;  $\text{AlBr}_3$ , 7727-15-3;  $\text{H}_2\text{AlBr}$ , 54844-46-1;  $\text{HAlBr}_2$ , 15576-93-9;  $\text{ZnCl}_2$ , 7646-85-7;  $\text{H}_3\text{Zn}_2\text{Cl}\cdot 0.35(\text{C}_2\text{H}_5)_2\text{O}$ , 54931-33-8;  $\text{ZnBr}_2$ , 7699-45-8;  $\text{H}_3\text{Zn}_2\text{Br}\cdot 0.29(\text{C}_2\text{H}_5)_2\text{O}$ , 54931-35-0;  $\text{ZnI}_2$ , 10139-47-6;  $\text{ZnI}_2\cdot\text{AlH}_3\cdot 1.79(\text{C}_2\text{H}_5)_2\text{O}$ , 54931-34-9;  $\text{CdBr}_2$ , 7789-42-6;  $\text{CuCl}$ , 7758-89-6.

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## Syntheses, Nuclear Magnetic Resonance Spectra, and Mass Spectra of the (Halomethyl)disilanes

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The (halomethyl)disilanes  $\text{XCH}_2\text{SiH}_2\text{SiH}_3$ , in which  $\text{X} = \text{Cl}$ ,  $\text{Br}$ , and  $\text{I}$ , have been synthesized and characterized. (Chloromethyl)disilane was prepared by the reaction of diazomethane with hexachlorodisilane, followed by  $\text{LiAlH}_4$  reduction of the  $\text{ClCH}_2\text{Si}_2\text{Cl}_5$  produced. (Bromomethyl)disilane was prepared by the direct reaction of bromodisilane with diazomethane. (Iodomethyl)disilane was isolated from the reaction of sodium iodide and (chloromethyl)disilane in acetone. The physical properties of these compounds are presented and correlated with the properties of related organic and organometallic compounds. The (halomethyl)disilanes represent a new type of series, the analogs of the propyl halides in which two of the carbon atoms have been replaced by silicon.

### Introduction

While many silicon-functional derivatives of silane have been prepared and characterized, much less information has been reported about the related carbon-functional alkylsilanes and -germanes. We have undertaken a study of related series of  $\text{XCH}_2\text{MH}_2\text{Y}$  ( $\text{M} = \text{Si}$ ,  $\text{Ge}$ ) compounds and have synthesized the (halomethyl)silanes<sup>1</sup> and -germanes,<sup>2</sup> the (methoxy-alkyl)silanes and -germanes,<sup>3</sup> and the (halomethyl)silylcobalt tetracarbonyls.<sup>3</sup> No carbon-functional disilanyl hydrides are known, and we here report the preparation of the (halomethyl)disilanes in order to ascertain the stability and properties of this series and to study the effects of chain extension by a  $-\text{SiH}_3$  group by comparison of these compounds

with the "parent"  $\text{XCH}_2\text{SiH}_3$  species.<sup>1,4</sup>

In addition, mass spectra of organic molecules and their analogs in which a carbon atom is replaced by a silicon show considerable differences. Interaction between a remote electron-rich center and silicon often leads to rearranged ions in which a bond forms between the silicon and the previously not directly bonded functional group. Such interaction has previously been postulated<sup>1,4</sup> for the "parent" (halomethyl)silanes, and it seemed of interest to examine the effect of  $-\text{SiH}_3$  chain extension by comparing the properties of  $\text{XCH}_2\text{SiH}_2-\text{H}$  and  $-\text{SiH}_3$  compounds.

Although the fluoroalkyl derivatives  $\text{FCH}_2\text{CH}_3$  and  $\text{FCH}_2\text{GeH}_3$ <sup>5</sup> are known, the corresponding silicon compound,

$\text{FCH}_2\text{SiH}_3$ , has not yet been successfully isolated, presumably due to its instability.<sup>1</sup> For this reason no attempt was made to prepare (fluoromethyl)disilane, and the term halogen (or X) as used here is restricted to Cl, Br, or I.

### Experimental Section

**General Apparatus and Techniques.** With the exception of the preparation of  $\text{CH}_2\text{N}_2$  and its use in the insertion reaction with  $\text{Si}_2\text{Cl}_6$ , all of the work in this investigation was carried out using standard vacuum techniques. Materials used in the syntheses were prepared by standard methods or obtained from commercial sources. Diazomethane was prepared by the thermal decomposition of EXR-101 (*N,N'*-dinitroso-*N,N'*-dimethylterephthalamide, 70% (wt/wt) in mineral oil), which was kindly donated by the Du Pont High Explosives Division.

Nuclear magnetic resonance data were obtained with a Varian Associates Model A-60A spectrometer. Chemical shifts were determined in 10% and 90% (v/v) cyclohexane solutions, plotted as a function of concentration, and extrapolated to infinite dilution. Mass spectra were obtained using a Du Pont Model 21-492 spectrometer operating at 75 eV and 50  $\mu\text{A}$ . Standard peak matching techniques were used to determine the exact masses. Gas-phase infrared spectra were obtained with a Perkin-Elmer Model 337 spectrometer. Temperatures below the range of mercury thermometers were measured by an iron-constantan thermocouple vs. an ice-water reference junction. Pressures were read from a mercury manometer with the aid of a cathetometer. Melting points were determined in vacuo by a Stock magnetic plunger.<sup>6</sup>

**Preparation of (Chloromethyl)disilane.** (Chloromethyl)disilane was prepared by reducing the  $\text{ClCH}_2\text{Si}_2\text{Cl}_5$  formed from the reaction of diazomethane and  $\text{Si}_2\text{Cl}_6$ . Diazomethane was generated by placing 200 g of 40% aqueous KOH (wt/wt) into a mechanically stirred 1-l. three-necked flask containing 20 g of EXR-101 and 300 ml of diethyl ether cooled to 0°. The surrounding ice bath was replaced by a heating mantle, and the vessel was slowly warmed to 34°. At this temperature both ether and the  $\text{CH}_2\text{N}_2$  formed by the thermal decomposition of the EXR-101 codistilled through a drying tube filled with KOH pellets and a water-cooled condenser into a 500-ml three-necked flask which was cooled to -45°. The 500-ml flask, which was equipped with a -78° condenser fitted with a  $\text{CaCl}_2$  drying tube, contained 22.12 g (8.22 mmol) of  $\text{Si}_2\text{Cl}_6$ , 0.5 g of Cu powder, 0.3 g of CuCl, and 80 ml of diethyl ether. After the ether- $\text{CH}_2\text{N}_2$  distillate became colorless, the products in the 500-ml flask were transferred to the vacuum line where the ether was removed by vacuum distillation at -45°. The material remaining was transferred in air to a 250-ml flask, 50 ml of *n*-butyl ether was added, and the vessel was evacuated. The contents of the vessel were kept at -15° and magnetically stirred while 4.83 g of  $\text{LiAlH}_4$  was added over a period of 3 hr. The products were removed when they exerted a pressure of 10 mm or more. The vessel was allowed to warm to room temperature overnight, and the products were again removed. The mixture of compounds from this reaction was fractionated at -95°, and the material collected at this temperature was subjected to distillation on a low-temperature still. (Chloromethyl)disilane, 4.50 g (4.06 mmol) or 49.5% yield based on  $\text{Si}_2\text{Cl}_6$ , was collected between -72 and -66°.

The Dumas molecular weight of (chloromethyl)disilane is 110.6 (calcd 110.7). The experimental exact mass of the  $^{37}\text{ClC}_1\text{Si}_2\text{H}_6^+ [(P-1)^+]$  ion is 110.96762 (calcd 110.96671; error 8.2 ppm). The vapor pressures for  $\text{ClCH}_2\text{Si}_2\text{H}_5$  over the temperature range -23 to +26° are given in Table I and are represented by the equation  $\log P_{\text{Torr}} = 1869.34/T(^{\circ}\text{K}) + 8.0714$ . Several points were remeasured at the conclusion of the experiment, and the good agreement of these points with previously determined vapor pressures indicates that essentially no decomposition occurred during this determination and thus  $\text{ClCH}_2\text{Si}_2\text{H}_5$  possesses a reasonable thermal stability at room temperature. The boiling point,  $\Delta H_{\text{vap}}$ , and Trouton's constant are calculated to be 87°, 8.55 kcal/mol, and 23.7 eu, respectively. The vapor pressure at 0° is 16.9 mm, and the melting point of (chloromethyl)disilane is -107.8°.

Infrared absorptions occur at 2935 (w), 2150 (vs), 1402 (w), 1173 (vw), 1098 (w), 992 (sh), 936 (s), 896 (sh), 887 (s), 823 (vs), 791 (sh), 782 (s), 763 (sh), 754 (sh), 674 (sh), 662 (w), 655 (sh), 626 (vw), and 500 (m)  $\text{cm}^{-1}$ .

**Preparation of (Bromomethyl)disilane.** (Bromomethyl)disilane was prepared by a methylene insertion into  $\text{Si}_2\text{H}_5\text{Br}$ , a reaction analogous to that described for (chloromethyl)disilane. Bromodisilane was

**Table I.** Vapor Pressure vs. Temperature Data for (Chloromethyl)disilane

$T, ^{\circ}\text{C}$	$P_{\text{obsd}}, \text{mm}$	$P_{\text{calcd}}, \text{mm}$	$P_{\text{obsd}} - P_{\text{calcd}}, \text{mm}$
26.3	67.6	67.6	0.0
26.2	67.0	67.3	-0.3
23.5	59.5	59.0	0.5
19.9	49.6	49.4	0.2
17.7	44.5	44.2	0.3
15.4	39.5	39.3	0.2
12.6	33.8	33.9	-0.1
9.0	27.9	28.0	-0.1
5.8	23.5	23.5	0.0
3.3	20.3	20.5	-0.2
0.0	16.8	17.0	-0.2
-3.1	14.4	14.1	0.3
-5.7	12.1	12.1	0.0
-10.2	9.0	9.2	-0.2
-23.2	4.0	3.9	0.1
0.0 <sup>a</sup>	16.8	17.0	-0.2
26.2 <sup>a</sup>	67.5	67.3	0.2

<sup>a</sup> Determined at the conclusion of the experiment.

recovered in up to 60% yield from the aluminum bromide catalyzed reaction of  $\text{Si}_2\text{H}_6$  with HBr, purified by trap-to-trap fractionation, and identified by its ir spectrum.<sup>7</sup> A 50% excess of  $\text{CH}_2\text{N}_2$  in ether, prepared as above, was vacuum distilled into a 1-l. flask containing 0.5 g (3.22 mmol) of bromodisilane, 0.5 g of Cu powder, and 0.2 g of CuCl. The reactants were allowed to warm to -50° and were held at that temperature for 45 min with magnetic stirring. The contents of the vessel were then separated by distillation on a low-temperature still. (Bromomethyl)disilane was collected at -48° in 50% yield based on the  $\text{BrSiH}_2\text{SiH}_3$  used. The exact mass of the  $^{79}\text{BrSi}_2\text{CH}_6^+ [(P-1)^+]$  ion is 152.919197 (calcd 152.919197; error 0.0 ppm). The vapor pressure of (bromomethyl)disilane at 0° is 6.6 Torr, and the melting point is -84.3°.

Infrared absorptions occur at 2952 (w), 2935 (w), 2851 (w), 2172 (sh), 2160 (vs), 2137 (sh), 2128 (sh), 1718 (w, b), 1590 (w), 1568 (w), 1456 (w), 1434 (w), 1380 (w), 1278 (vw, b), 1125 (vw), 1055 (vw), 1050 (vw), 931 (sh), 890 (sh), 883 (s), 821 (sh), 818 (s), 813 (sh), 806 (sh), 784 (s), 778 (sh), 761 (sh), 592 (vw), and 492 (w)  $\text{cm}^{-1}$ .

It should be noted that if the contents of the reaction vessel were not fractionated but were reduced with  $\text{LiAlH}_4$  in butyl ether, methylidisilane was obtained in 87% yield. The reduction was allowed to proceed for 1.5 hr during which time the temperature of the vessel rose slowly from -15 to +20°. Methylidisilane was separated by trap-to-trap fractionation and identified by its previously reported<sup>8</sup> ir spectrum, vapor pressure (381.5 Torr at 0°; lit. 382.6 Torr), and PMR spectrum.<sup>7</sup>

**Preparation of (Iodomethyl)disilane.** (Iodomethyl)disilane was prepared by the reaction of 0.938 g (8.38 mmol) of (chloromethyl)disilane with 2.50 g (16.7 mmol) of sodium iodide in 7 ml of acetone. After 1.5 hr at room temperature fractionation of the mixture gave 1.58 g (7.83 mmol) of (iodomethyl)disilane, a 92% yield. The compound passed through a trap maintained at -23° and stopped in a trap held at -45°; the compound was then distilled from a low-temperature column just prior to the determination of its physical properties. The experimental exact mass of the molecular ion  $\text{P}^+$  is 201.9127 (calcd 201.9131; error 2.0 ppm). The melting point and vapor pressure at 0° of  $\text{ICH}_2\text{Si}_2\text{H}_5$  are -57.7° and 2.3 Torr, respectively.

Infrared absorptions occur at 2934 (w), 2144 (vs), 2133 (s), 1369 (w), 1288 (w, b), 1068 (vw), 1010 (w), 1002 (w), 932 (sh), 928 (s), 923 (sh), 885 (sh), 878 (s), 866 (sh), 805 (vs), 797 (vs), 782 (s), 776 (s), 750 (m), 720 (w), 712 (w), and 494 (w)  $\text{cm}^{-1}$ .

### Results and Discussion

It has been reported that methylene insertion into metal-bromine bonds to form (bromomethyl)metal compounds proceed with higher yields than the corresponding insertions into metal-chlorine bonds.<sup>9</sup> We have not observed this higher yield in our studies. We have observed, however, that after  $\text{LiAlH}_4$  reduction the yield of (bromomethyl)metal hydride recovered is often much lower than that of the corresponding

**Table II.** Proton Magnetic Resonance Data for (Halomethyl)disilane

Compd	Chem shifts at infinite dilution, $\tau$		
	CH <sub>2</sub>	SiH <sub>2</sub>	SiH <sub>3</sub>
ClCH <sub>2</sub> SiH <sub>2</sub> SiH <sub>3</sub>	7.07	6.02	6.72
BrCH <sub>2</sub> SiH <sub>2</sub> SiH <sub>3</sub>	7.44	5.78	6.72
ICH <sub>2</sub> SiH <sub>2</sub> SiH <sub>3</sub>	7.96	5.37	6.72

Compd	Coupling constants, Hz			
	$J_{\text{H-H}'}$ (SiH <sub>2</sub> )	$J_{\text{H-H}'}$ (SiH <sub>3</sub> )	$J^{29}\text{Si-H}$ (SiH <sub>2</sub> )	$J^{29}\text{Si-H}$ (SiH <sub>3</sub> )
ClCH <sub>2</sub> SiH <sub>2</sub> SiH <sub>3</sub>	3.7	3.0	200.6	199.8
BrCH <sub>2</sub> SiH <sub>2</sub> SiH <sub>3</sub>	3.9	3.0	200.7	199.9
ICH <sub>2</sub> SiH <sub>2</sub> SiH <sub>3</sub>	4.2	2.9	201.2	199.8

(chloromethyl)metal hydride. For example, the yields of (bromomethyl)germane<sup>2</sup> and (bromomethyl)silane<sup>1</sup> prepared by a diazomethane methylene insertion into GeBr<sub>4</sub> and SiBr<sub>4</sub>, followed by LiAlH<sub>4</sub> reduction, were only 40% and 8%, respectively, while the analogous procedure gave higher yields of the corresponding chloromethyl compounds. By allowing diazomethane to react directly with the hydride BrSi<sub>2</sub>H<sub>5</sub> and eliminating the necessity for a LiAlH<sub>4</sub> reduction, we were able to obtain (bromomethyl)disilane in the surprisingly good yield of 50%, a yield identical with that found for (chloromethyl)disilane. Perhaps the lower overall yield of bromide in the cases cited above is a reflection of the greater ease with which the C-Br bond is reduced compared to the C-Cl bond.

While we experienced no difficulties in handling diazomethane as a codistillate with diethyl ether, it should be emphasized that CH<sub>2</sub>N<sub>2</sub> is extraordinarily toxic and has been reported to decompose to polymethylene and nitrogen with explosive violence. During the preparation of (bromomethyl)disilane the pressure in the vacuum line was observed to increase continuously with the deposition of a white polymeric material, especially in the vicinity of glass joints and stopcocks.

The (halomethyl)disilanes are colorless liquids which are air and water sensitive. They burn in air with a smoky flame, as would be expected for Si<sub>2</sub>H<sub>5</sub> compounds, and are pyrophoric, but only mildly so. They are soluble in, and inert toward, the common hydrocarbon and ethereal solvents, as well as acetone. Although the neat compounds are fairly stable at room temperature over a short period of time, as demonstrated by the vapor pressure determination of ClCH<sub>2</sub>Si<sub>2</sub>H<sub>5</sub>, at slightly elevated temperatures the (halomethyl)disilanes rearrange to yield the isomeric silicon-functional 1-halo-1-methyldisilanes.<sup>3</sup>

**Proton NMR Spectra.** For each of the (halomethyl)disilanes, the spectra were found to be first order with integrated peak area ratios within 1.5% of the expected values. The proton chemical shifts and coupling constants are presented in Table II.

The chemical shifts of the ( $\alpha$ ) XCH<sub>2</sub> protons are, as expected, linearly related to the electronegativity of the halogen substituent. This relationship can be represented by the equation  $\tau = -1.82\chi + 12.80$ , where  $\chi$  is the Huggins electronegativity of the halogen. The chemical shifts of the ( $\beta$ ) SiH<sub>2</sub> protons vary in the opposite direction, an anisotropy effect commonly observed. The chemical shifts of the ( $\gamma$ ) SiH<sub>3</sub> protons, as well as the <sup>29</sup>Si-H and vicinal H-H' coupling constants for the protons, are essentially invariant with change in halogen, which suggests that the effect of the halogen is completely attenuated through the four intermediary bonds. Table III summarizes the methylene chemical shifts for compounds of the type XCH<sub>2</sub>Y in which X represents a halide and Y represents hydrogen, or a silicon or germanium hydride.

It can be seen from these data that the chemical shifts of the CH<sub>2</sub> protons are essentially unaffected if a proton of a methyl halide is replaced by a silyl or a disilyl group; and

**Table III.** Chemical Shifts ( $\tau$ ) in XCH<sub>2</sub>Y Compounds

	$\alpha$ Protons			
	H <sup>a</sup>	SiH <sub>3</sub> <sup>a</sup>	SiH <sub>2</sub> SiH <sub>3</sub> <sup>b</sup>	GeH <sub>3</sub> <sup>c</sup>
ClCH <sub>2</sub>	7.04	7.06	7.07	6.94
BrCH <sub>2</sub>	7.41	7.42	7.44	7.37
ICH <sub>2</sub>	7.96	7.94	7.96	7.90

	$\beta$ Protons	
	SiH <sub>3</sub> <sup>a</sup>	SiH <sub>2</sub> SiH <sub>3</sub> <sup>b</sup>
ClCH <sub>2</sub>	6.19	6.02
BrCH <sub>2</sub>	5.94	5.78
ICH <sub>2</sub>	5.49	5.37

<sup>a</sup> Reference 1. <sup>b</sup> This work. <sup>c</sup> Reference 2.

**Table IV.** Mass Spectral Fragmentation Pattern of (Chloromethyl)disilane

<i>m/e</i>	% rel abund	Mass assignment	
109	29.0	<sup>37</sup> ClCSi <sub>2</sub> H <sub>4</sub> <sup>+</sup>	<sup>35</sup> ClCSi <sub>2</sub> H <sub>6</sub> <sup>+</sup>
108	18.8	<sup>37</sup> ClCSi <sub>2</sub> H <sub>3</sub> <sup>+</sup>	<sup>35</sup> ClCSi <sub>2</sub> H <sub>5</sub> <sup>+</sup>
107	32.4	<sup>37</sup> ClCSi <sub>2</sub> H <sub>2</sub> <sup>+</sup>	<sup>35</sup> ClCSi <sub>2</sub> H <sub>4</sub> <sup>+</sup>
106	34.0	<sup>37</sup> ClCSi <sub>2</sub> H <sup>+</sup>	<sup>35</sup> ClCSi <sub>2</sub> H <sub>3</sub> <sup>+</sup>
105	21.8	<sup>37</sup> ClCSi <sub>2</sub> <sup>+</sup>	<sup>35</sup> ClCSi <sub>2</sub> H <sub>2</sub> <sup>+</sup>
81	35.3	<sup>37</sup> ClCSiH <sub>4</sub> <sup>+</sup>	
80	14.3	<sup>37</sup> ClCSiH <sub>3</sub> <sup>+</sup>	<sup>35</sup> ClCSiH <sub>5</sub> <sup>+</sup>
79	100.0	<sup>37</sup> ClCSiH <sub>2</sub> <sup>+</sup>	<sup>35</sup> ClCSiH <sub>4</sub> <sup>+</sup>
78	21.6	<sup>37</sup> ClCSiH <sup>+</sup>	<sup>35</sup> ClCSiH <sub>3</sub> <sup>+</sup>
69	20.1		CSi <sub>2</sub> H <sup>+</sup>
65 (R)	39.4	<sup>37</sup> ClSiH <sub>2</sub> <sup>+</sup> (R)	<sup>35</sup> ClSiH <sub>2</sub> <sup>+</sup> (R)
63 (R)	86.0		<sup>35</sup> ClSi <sup>+</sup> (R)
44	17.8		CSiH <sub>4</sub> <sup>+</sup>
43	34.6		CSiH <sub>3</sub> <sup>+</sup>
42	27.9		CSiH <sub>2</sub> <sup>+</sup>

**Table V.** Mass Spectral Fragmentation Pattern of (Bromomethyl)disilane

<i>m/e</i>	% rel abund	Mass assignment	
155	13.5		<sup>81</sup> BrCSi <sub>2</sub> H <sub>6</sub> <sup>+</sup>
153	20.2	<sup>79</sup> BrCSi <sub>2</sub> H <sub>6</sub> <sup>+</sup>	<sup>81</sup> BrCSi <sub>2</sub> H <sub>4</sub> <sup>+</sup>
152	18.0	<sup>79</sup> BrCSi <sub>2</sub> H <sub>5</sub> <sup>+</sup>	<sup>81</sup> BrCSi <sub>2</sub> H <sub>3</sub> <sup>+</sup>
151	15.4	<sup>79</sup> BrCSi <sub>2</sub> H <sub>4</sub> <sup>+</sup>	<sup>81</sup> BrCSi <sub>2</sub> H <sub>2</sub> <sup>+</sup>
150	13.1	<sup>79</sup> BrCSi <sub>2</sub> H <sub>3</sub> <sup>+</sup>	
125	56.4		<sup>81</sup> BrCSiH <sub>4</sub> <sup>+</sup>
124	20.7		<sup>81</sup> BrCSiH <sub>3</sub> <sup>+</sup>
123	60.1	<sup>79</sup> BrCSiH <sub>4</sub> <sup>+</sup>	<sup>81</sup> BrCSiH <sub>2</sub> <sup>+</sup>
122	17.3	<sup>79</sup> BrCSiH <sub>3</sub> <sup>+</sup>	
109 (R)	62.1	<sup>79</sup> BrSiH <sub>2</sub> <sup>+</sup> (R)	<sup>81</sup> BrSi <sup>+</sup> (R)
107 (R)	57.8	<sup>79</sup> BrSi <sup>+</sup> (R)	
74	10.6		CSi <sub>2</sub> H <sub>6</sub> <sup>+</sup>
73	10.1		CSi <sub>2</sub> H <sub>5</sub> <sup>+</sup>
69	20.2		CSi <sub>2</sub> H <sup>+</sup>
45	57.7		SiCH <sub>5</sub> <sup>+</sup>
44	78.8		SiCH <sub>4</sub> <sup>+</sup>
43	100.0		SiCH <sub>3</sub> <sup>+</sup>
42	14.1		SiCH <sub>2</sub> <sup>+</sup>

in the case of the replacement of a proton by a germyl group, the methylene protons are only slightly deshielded. Similarly, the substitution of a silyl group for a proton in the  $\beta$  position has essentially no effect on the chemical shifts of the  $\alpha$  protons; however, the  $\beta$  protons in (halomethyl)disilanes are consistently deshielded ( $-0.14 \pm 0.03$  ppm) relative to the shorter chain homologs, the (halomethyl)silanes.

**Mass Spectra.** For the (halomethyl)disilanes the assignments and intensities of those ions present in greater than 10% abundance relative to the most abundant or base peak are presented in Tables IV-VI.

In addition to peaks for the molecular or "parent" ion P<sup>+</sup> or ions derived from the molecular ion by the loss of any number of hydrogen atoms (P - nH)<sup>+</sup> and their expected fragmentation products, each spectrum contains peaks due to the rearrangement ions XSiH<sub>n</sub><sup>+</sup> and XSi<sub>2</sub>H<sub>n+1</sub><sup>+</sup>. Such ions are labeled (R) in Tables IV-VI. The formation of these

Table VI. Mass Spectral Fragmentation Pattern of (Iodomethyl)disilane

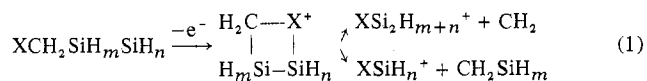
<i>m/e</i>	% rel abund	Mass assignment
202	11.4	ICS <sub>2</sub> H <sub>7</sub> <sup>+</sup>
171	75.8	ICSiH <sub>4</sub> <sup>+</sup>
170	66.1	ICSiH <sub>3</sub> <sup>+</sup>
155 (R)	53.2	ISI <sup>+</sup> (R)
76	12.9	
75	100.0	CSi <sub>2</sub> H <sub>7</sub> <sup>+</sup>
74	12.4	CSi <sub>2</sub> H <sub>6</sub> <sup>+</sup>
73	49.6	CSi <sub>2</sub> H <sub>5</sub> <sup>+</sup>
72	11.9	CSi <sub>2</sub> H <sub>4</sub> <sup>+</sup>
71	16.3	CSi <sub>2</sub> H <sub>3</sub> <sup>+</sup>
70	10.3	CSi <sub>2</sub> H <sub>2</sub> <sup>+</sup>
69	32.2	CSi <sub>2</sub> H <sup>+</sup>
44	20.1	CSiH <sub>4</sub> <sup>+</sup>
43	18.7	CSiH <sub>3</sub> <sup>+</sup>
42	97.6	CSiH <sub>2</sub> <sup>+</sup>
41	13.6	CSiH <sup>+</sup>

Table VII. Percent of the Total Ion Current, Σ<sub>m</sub>, Carried by P<sup>+</sup> and (P - nH)<sup>+</sup> Ions

Compd	X = Cl	X = Br	X = I
C <sub>2</sub> H <sub>5</sub> X <sup>a</sup>	40.3	61.1	68.3
<i>n</i> -C <sub>3</sub> H <sub>7</sub> X <sup>a</sup>	3.0	10.5	38.3
<i>n</i> -C <sub>4</sub> H <sub>9</sub> X <sup>a</sup>	0.33	5.1	17.9
GeH <sub>2</sub> CH <sub>2</sub> X <sup>b</sup>	10.5	17.2	24.2
SiH <sub>3</sub> CH <sub>2</sub> X <sup>c</sup>	19.6	16.9	19.2
Si <sub>2</sub> H <sub>5</sub> CH <sub>2</sub> X <sup>d</sup>	22.6	12.1	5.9

<sup>a</sup> Reference 11. <sup>b</sup> Reference 2. <sup>c</sup> Reference 1. <sup>d</sup> This work.

rearranged ions suggests the intermediacy of a cyclic species derived from one or more of the (P - nH)<sup>+</sup> ions, followed by the loss of a neutral CH<sub>2</sub> or CH<sub>2</sub>SiH<sub>*m*</sub> fragment, as indicated in eq 1.



The formation of a fairly stable cyclic species has been observed to yield enhanced ion intensities in many systems,<sup>10</sup> and the relative intensities of the rearrangement ions are considerable in the (halomethyl)disilanes (although the rearrangement ions in these compounds are not the most intense ions in the spectra as is the case with the (halomethyl)silanes<sup>1</sup>). In an attempt to evaluate whether a cyclic species was of only momentary existence in effecting the transfer of halogen from carbon to silicon or was of a greater stability, we compared the percentage of the total ion current carried by ions P<sup>+</sup> and (P - nH)<sup>+</sup> in which the heavy-atom skeleton of the molecule had been preserved. This information is summarized in Table VII for the alkyl halides,<sup>11</sup> the (halomethyl)germanes,<sup>2</sup> the (halomethyl)silanes,<sup>5</sup> and the (halomethyl)disilanes. All ions present in greater than 1% relative abundance have been included in the calculation. Because the fragmentation patterns of a compound are somewhat dependent upon the type of spectrometer used and also because the intensity of the molecular ion compared to that of the (P - nH)<sup>+</sup> ions varies with the type of heteroatoms contained in the skeleton,<sup>12</sup> the trends in the data provide the most meaningful information.

It can be seen from Table VII that the values for the alkyl halides illustrate two trends: (1) as the chain length increases, the fraction of the ion current carried by P<sup>+</sup> and (P - nH)<sup>+</sup> decreases; (2) the intensity of the molecular ion plus the (P - nH)<sup>+</sup> ions varies in the order I > Br > Cl. The (halomethyl)germanes vary in this same manner. The (halomethyl)silanes and -disilanes, however, do not reflect this trend, and in the case of the (halomethyl)disilanes, Σ<sub>m</sub> varies in the opposite order, i.e., Cl > Br > I. Some effect, then, appears to stabilize the (P - nH)<sup>+</sup> ions in the cases of (chloromethyl)silane, (chloromethyl)disilane, and to a lesser extent

(bromomethyl)disilane. This effect is consistent with the formation of a cyclic intermediate. McLafferty<sup>11</sup> has also noted that for compounds in which a cyclic species is postulated, those involving a chlorine or a bromine are more stable than those involving iodine. The detection of significant rearranged ion fragments, therefore, is consistent with the cyclic intermediate having sufficient stability to effect the transfer of halogen from carbon to silicon.

Mass spectral interactions between remote centers in organosilicon compounds and the silicon atom itself have been studied by Weber et al.,<sup>13-15</sup> who have postulated transannular interactions in such species.<sup>15</sup> It has been suggested that dipole moment,<sup>4</sup> mass spectral,<sup>1</sup> and other evidence is consistent with interactions between the nondirectly bonded halogen and silicon in the parent (halomethyl)silanes, and the presence of rearrangement ions in the mass spectra of the (halomethyl)disilanes could also be so regarded. Weber<sup>13</sup> has also suggested that silicon can form a pentacoordinate transition state by use of its 3d orbitals in rearrangements involving transfer of a methoxy group to silicon. Although the mechanism of the rearrangements of electron-rich substituents to silicon has not been clearly established, it is evident that the (halomethyl)disilanes also participate in this phenomenon.

It must be noted, however, that cyclic intermediates can be formed with other than a halogen-silicon interaction. McLafferty<sup>11</sup> has suggested that the surprising abundance of C<sub>4</sub>H<sub>8</sub>X<sup>+</sup> ions in C<sub>6</sub> to C<sub>12</sub> alkyl halides can be attributed to the stability of five-membered rings, although for chain lengths of less than C<sub>6</sub> alkyl halides, the cyclic intermediates are thought to be unimportant.

The question of the optimum ring size for organosilicon rearrangements has attracted considerable attention. Weber<sup>14</sup> has suggested that migration of a trimethylsilyl group from a saturated alkyl carbon to a phenyl ring is important only when a six-membered ring transition state is possible. In a study of compounds similar to (halomethyl)disilanes, it was suggested<sup>3</sup> that in (methoxyalkyl)silanes, CH<sub>3</sub>O(CH<sub>2</sub>)<sub>*n*</sub>SiH<sub>3</sub>, a ring size of at least 5 is favored in the transition state. Djerassi and coworkers,<sup>16</sup> on the other hand, found that various trimethylsilyl ethers showed an insensitivity toward ring size (five to eleven membered) in the cyclic transition state, and White and McCloskey<sup>17</sup> have also noted an apparent lack of preference for a fixed ring size in cyclic intermediates involving transfer of a trimethylsilyl group. It is evident that in the (halomethyl)disilanes the size of a cyclic transition state cannot approach a five- or six-membered ring without the formation of dimeric species for which there is no direct evidence. It should be noted that thermal rearrangements of XCH<sub>2</sub>SiH<sub>2</sub>SiH<sub>3</sub> compounds produce a transfer of halogen to the silicon atom located in the β rather than the γ position.<sup>3</sup> Thus, it is evident that a comparison of stability as a function of ring size or organosilicon hydride derivatives must await a study of longer polysilane chains.

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**Registry No.** CH<sub>2</sub>N<sub>2</sub>, 334-88-3; Si<sub>2</sub>Cl<sub>6</sub>, 13465-77-5; ClCH<sub>2</sub>SiH<sub>2</sub>SiH<sub>3</sub>, 54713-74-5; BrSiH<sub>2</sub>SiH<sub>3</sub>, 13819-07-3; BrCH<sub>2</sub>SiH<sub>2</sub>SiH<sub>3</sub>, 54713-75-6; ICH<sub>2</sub>SiH<sub>2</sub>SiH<sub>3</sub>, 54713-76-7.

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## Synthesis and Base Strengths of Some ( $\omega$ -Methoxyalkyl)silanes and -germanes

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In an attempt to determine to what extent an electron-rich substituent is affected by a group 4 metal atom when not directly bonded to that metal atom, we have synthesized three series of compounds of the type  $MH_3(CH_2)_nOCH_3$  in which  $M = C, Si, \text{ and } Ge$  and  $n = 1-6$ . A comparison of their base strengths (proton affinities) as measured by the shift in the infrared OH stretching frequency of methanol upon complexation with the ethers shows that some factor(s) other than inductive effects significantly influences the electron-donating ability of oxygen in the silicon and germanium hydrides when  $n = 1$  and 2. At  $n = 3-6$ , however, the basicities of these ethers converge toward those of the carbon analogs. The silicon and germanium compounds not previously known have been characterized by infrared, proton magnetic resonance, and mass spectra, vapor pressure data, and melting points.

### Introduction

It is well documented that certain properties of organo-metallic compounds which contain a group 4 metal atom directly bonded to a potential electron donor are often anomalous compared to those of the carbon analogs.<sup>1</sup> Data from studies involving magnetic susceptibility,<sup>2</sup> dipole moments,<sup>3</sup> basicity,<sup>4-6</sup> bond lengths and bond angles,<sup>7</sup> and various kinds of spectra<sup>8,9</sup> have shown that many properties of organosilanes and -germanes are influenced by effects not evident in their carbon analogs. It has been suggested that these deviations are caused by an interaction which may be occurring between available vacant d orbitals on the group 4 metal atom (Si, Ge) and the lone pair of electrons on the directly bound donor atom (O, N, F).<sup>10</sup> The existence of a similar interaction between these atoms when they are not directly bound but separated by an intervening methylene group has also been suggested.<sup>11</sup> In the case of the  $SiH_3CH_2X$  compounds ( $X = \text{halogen}$ ) the constancy of the dipole moments has been ascribed to the delocalization of electron density from the halogen to the silicon, an intramolecular interaction which decreases from Cl to Br to I.<sup>3</sup> There is little agreement, however, as to whether such anomalies in organosilicon hydrides cease when the donor substituent is beyond the  $\beta$  position; and too few data are available to assess the situation for organogermanium hydrides. We have, therefore, prepared a series of homologous ( $\omega$ -methoxyalkyl)silanes and also ( $\omega$ -methoxyalkyl)germanes in order to compare their properties to each other and to those of the appropriate carbon analogs in which no effects other than inductive are believed to occur.

The parameters chosen as indicative of possible donor-metal interaction were the base strengths of the  $MH_3(CH_2)_nOCH_3$  compounds ( $M = C, Si, Ge; n = 0-6$ ) and the PMR chemical shifts and coupling constants. Base strengths were determined by measuring the difference in the infrared spectra between the O-H stretching frequency of methanol when free and when hydrogen bonded to the group 4 ether. This shift has been shown to be directly related to the base strength of the ether<sup>12</sup>

and presumably the electron availability on the Lewis base.

### Experimental Section

**Apparatus and Techniques.** All synthetic work was carried out in a borosilicate glass vacuum system using standard vacuum techniques. Mass spectral data were obtained with a Du Pont Model 21-492 double-focusing spectrometer operating at 75 eV and 50  $\mu$ A. PMR parameters were measured with a Varian Associates A-60A instrument whose probe temperature was 35°. Vapor-phase ir spectra were recorded using a 10-cm cell with KBr windows. Melting points were determined with a Stock magnetic plunger. Pressures were obtained using a mercury manometer which was read with the aid of a cathetometer. Temperatures beyond the range of the mercury thermometer were measured using an iron-constantan thermocouple with an ice-water reference junction.

Shifts in the stretching frequency between free and hydrogen-bonded O-H ( $\Delta\nu$ ) were obtained with a Perkin-Elmer Model 421 grating spectrophotometer using linear scan ( $cm^{-1}$ ). Typically, methanol and the ether of interest were condensed with either  $C_6H_{12}$  or  $CCl_4$  as solvent to form a solution 0.02  $M$  in MeOH and 0.2  $M$  in ether. The resulting mixture was removed by means of a syringe through a serum cap and immediately injected into a 1-mm fixed-distance sodium chloride cell. A mixture containing only 0.2  $M$  ether in the appropriate solvent was similarly placed in a matched cell for use as reference. A minimum of three spectra were recorded. No variation in  $\Delta\nu$  was observed when the ether concentration was varied from 0.2 to 0.005  $M$  while holding the methanol concentration at 0.02  $M$ ; similarly, the  $\Delta\nu$  remained constant when the MeOH concentration was varied from 0.2 to 0.005  $M$  with the ether concentration at 0.2  $M$ .

**Syntheses.** The reference alkyl methyl ethers were synthesized by reaction of the appropriate 1-chloroalkane with  $NaOCH_3$ . Compounds of the  $SiH_3(CH_2)_nOCH_3$  series in which  $n = 2, 4, \text{ and } 6$  and those of the series  $GeH_3(CH_2)_nOCH_3$  in which  $n = 2, 3, 4, \text{ and } 6$  were prepared by the general reaction of  $KSiH_3$  or  $KGeH_3$  with the appropriate 1-haloalkyl methyl ether. Typically, 5 ml of hexamethylphosphotriamide (Fisher) in a 100-ml flask was degassed, refluxed under vacuum pumping for 10 min, and then cooled with an ice bath. The vessel was subsequently opened to the air, potassium (2.6 mg-atoms) was added, and the vessel was rapidly reevacuated. Silane or germane (2.7 mmol) was condensed into the flask and the