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SYNTHESIS AND PROTON NUCLEAR MAGNETIC RESONANCE SPECTRA OF SILYLMETHYL HALIDES

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SUMMARY

The new compounds SiH_3CH_2Br and SiH_3CH_2I have been synthesized and characterized. Their proton NMR spectra and that of SiH_3CH_2Cl have been examined and compared with those of the isomeric halides, CH_3SiH_2X, ($X=Cl$, Br, I).

INTRODUCTION

A study of the similarities and differences between the linkage formed by carbon to a given element and that formed by silicon to the same element has been the subject of numerous investigations. However, to the best of the authors' knowledge, no comparative studies have ever been performed on a series of carbon-functional organosilicon compounds and the isomeric series of silicon-functional compounds. The simplest series of this type are those derived from methylsilane, CH_3SiH_3; *i.e.*, the series composed of the carbon-functional silylmethyl halides** [(halomethyl)silanes], SiH_3CH_2X, and the series composed of the isomeric silicon functional methylsilyl halides** [halomethylsilanes], CH_3SiH_2X.

A study of the former series, in which X represents a halogen, was carried out in this investigation since it was felt to present considerable potential interest, especially in view of the fact that the isomeric CH_3SiH_2X[1] series and the end-members of the series, CH_3–CH_2–X[2] and SiH_3–SiH_2–X[3] have been well characterized.

EXPERIMENTAL

Apparatus and techniques

All work was carried out in a borosilicate (Pyrex) glass vacuum system. The apparatus and techniques were similar to those previously described[4]. Mass spectra were measured by means of a Consolidated Electrodynamics Corporation Model 21-130 mass spectrometer operating at an ionizing voltage of 76.0 eV and at an ionizing current of 20 μA. Infrared spectra were obtained with a Perkin–Elmer Model

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** Because the names of the isomers are indistinguishable verbally when the standard nomenclature [given in brackets] is used, the use of the name silylmethyl halide for the carbon-functional series, SiH_3-CH_2X, and methylsilyl halide for the silicon-functional series, CH_3SiH_2X, is preferred.

TABLE 1

MASS SPECTRAL FRAGMENTATION PATTERN FOR SiH_3CH_2X (X = Cl, Br, I)

SiH_3CH_2Cl			SiH_3CH_2Br			SiH_3CH_2I		
m/e	Intensity[a] (%)	Possible ion assignment[c]	m/e	Intensity[a] (%)	Possible ion assignment[c]	m/e	Intensity[a] (%)	Possible ion assignment[c]
28	66[b]	Si^+, N_2^{+}[b]	28	49[b]	Si^+, N_2^{+}[b]	28	75[b]	Si^+, N_2^{+}[b]
29	28	SiH^+	29	26	SiH^+	29	25	SiH^+
30	10	SiH_2^+	30	10	SiH_2^+	30	19	SiH_2^+
31	34	SiH_3^+	31	17	SiH_3^+	31	20	SiH_3^+
41	15	$SiCH^+$	41	17	$SiCH^+$	41	22	$SiCH^+$
42	17	$SiCH_2^+$	42	19	$SiCH_2^+$	42	31	$SiCH_2^+$
43	96	$SiHCH_2^+$	43	100	$SiHCH_2^+$	43	100	$SiHCH_2^+$
44	95[b]	$SiH_2CH_2^+$, CO_2^{+}[b]	44	55[b]	$SiH_2CH_2^+$, CO_2^{+}[b]	44	34[b]	$SiH_2CH_2^+$, CO_2^{+}[b]
45	13	$SiH_3CH_2^+$	45	19	$SiH_3CH_2^+$	45	94	$SiH_3CH_2^+$
63	81	$Si^{35}Cl^+$ (R)[d]	107	19	$Si^{79}Br^+$ (R)[d]	127	15	I^+
65	100	$SiH_2{}^{35}Cl^+$, $Si^{37}Cl^+$ (R)[d]	109	24	$SiH_2{}^{79}Br^+$, $Si^{81}Br^+$ (R)[d]	155	61	SiI^+ (R)[d]
67	25	$SiH_2{}^{37}Cl^+$ (R)[d]	111	14	$SiH_2{}^{81}Br^+$ (R)[d]	157	14	SiH_2I^+ (R)[d]
77	11	$SiCH_2{}^{35}Cl^+$	123	19	$SiH_2CH_2{}^{79}Br^+$, $SiCH_2{}^{81}Br^+$	171	75	$SiH_2CH_2I^+$
79	70	$SiH_2CH_2{}^{35}Cl^+$	124	20	$SiH_3CH_2{}^{79}Br^+$, $SiHCH_2{}^{81}Br^+$	172	13	$SiH_3CH_2I^+$
80	22	$SiH_3CH_2{}^{35}Cl^+$	125	18	$SiH_2CH_2{}^{81}Br^+$			
81	23	$SiH_2CH_2{}^{37}Cl^+$	126	19	$SiH_3CH_2{}^{81}Br^+$			

[a] Only fragments having an abundance of at least 10% relative to the most intense peak are considered. [b] The 28 and 44 m/e intensities are probably not reliable because of a leak in the inlet system of the mass spectrometer which could have allowed N_2 (mass = 28) and CO_2 (mass = 44) into the system. [c] Isotopic species are not considered except for $^{35}Cl/^{37}Cl$, and $^{79}Br/^{81}Br$. [d] The symbol (R) represents rearranged fragments.

137-B "Infracord" or a Model 521 double beam grating spectrophotometer using a 10 cm gas cell fitted with KBr windows. Elemental analyses were performed by Schwarzkopf Micro-analytical Laboratory, Woodside, N.Y.

SiH_3CH_2F

Attempts to synthesize this compound were unsuccessful. The reaction of gaseous SiH_3CH_2I with AgF at room temperature yielded a mixture of products, which, from the IR spectrum, appeared to consist chiefly of SiF_4 and CH_2F_2. Similarly, the use of other fluorides with SiH_3CH_2I or SiH_3CH_2Cl under various conditions did not produce the desired compound.

SiH_3CH_2Cl

This compound was synthesized by preparing and subsequently reducing $SiCl_3CH_2Cl$ as previously described[5].

Physical properties which had not been reported previously were measured. A freshly distilled sample (mol.wt. found 80.4, calcd. 80.6) melted sharply at $-89.6°$. Although a vapor pressure equation had previously been given for SiH_3CH_2Cl[5], the relationship was redetermined in this study. The vapor pressure equation and related data were found to be in good agreement with that reported previously, *viz.*, log $P_{mm} = -1528.06/(t+273.16)+7.89270$; heat of vaporization, 6.99 kcal·mole^{-1}; Trouton's constant, 22.9 kcal·mole^{-1}·deg^{-1}; extrapolated boiling point, 31.7°. The reproducibility of the vapor pressure curve on increasing the temperature (to a maximum temperature of $-16.0°$) and then decreasing the temperature in a glass-mercury tensimeter during a 14 h experiment showed that no detectable decomposition had occurred. This was confirmed by the observation that the IR spectrum and the mol.wt. of the sample underwent no change during the experiment.

TABLE 2

INFRARED SPECTRA OF SiH_3CH_2X (X = Cl, Br, I)

Band location (cm^{-1})			Vibration	Designation	Intensity
X=Cl	X=Br	X=I			
2950	2955	2962	C–H stretching	ν_1	m
2939	2945	2951	C–H stretching	ν_{12}	m
2187	2187	2190	Si–H stretching	ν_{13}	s
2165	2160	2162	Si–H stretching	ν_2	s
2153	2149	2153	Si–H stretching	ν_3	s
1412	1388	1383	CH_2 scissors	ν_4	m
1176	1118	1076	CH_2 wagging	ν_5	w
1107	1054	1012	CH_2 twisting	ν_{14}	w
948	952	952	SiH_3 deformation	ν_6, ν_7, ν_{15}	vs
933	930	925			vs
924	920	919			vs
814	798	788	CH_2 rocking	ν_{16}	m
767	737	734	Si–C stretching	ν_8	w
720	678	657	C–X stretching	ν_9	m
538	497	453	SiH_3 rocking	ν_{10}, ν_{17}	m
[a]	[a]	[a]	SiH_3 torsion	ν_{11}	
[a]	[a]	[a]	Si–C–X deformation	ν_{18}	

[a] Not observed.

The mass spectrum of SiH_3CH_2Cl was consistent with its proposed structure. Possible assignments of the major fragments (>10% relative abundance) observed are given in Table 1. A strong parent ion peak and several rearranged fragments were observed. Many of the *m/e* values could also be assigned in part to a different ion which, *e.g.*, contained an isotope other than that indicated. Absorption maxima, assignments, and intensities of the IR spectrum are given in Table 2. The spectrum of SiH_3CH_2Cl is reproduced in Fig. 1.

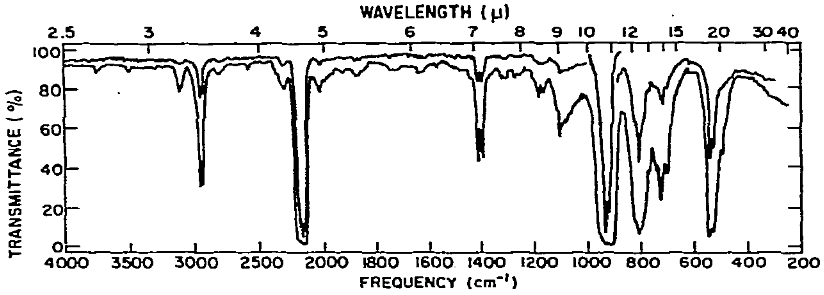


Fig. 1. Infrared spectrum of SiH_3CH_2Cl (p=75, 9, 4 mm).

SiH_3CH_2Br

The unmeasured quantity of $SiBr_3CH_2Br$, prepared from 10 g (28 mmoles) of $SiBr_4$ according to the method of Yakubovitch[6] was mixed with 10 ml of $(n\text{-}C_4H_9)_2O$ in a 250 ml flask fitted with a ground glass joint. To this was added a slurry of 4.7 g (125 mmoles) of $LiAlH_4$ in 125 ml of $(n\text{-}C_4H_9)_2O$ while the flask was cooled in an ice/rock salt bath. After stirring for 90 min at 0° the volatile materials were distilled into the vacuum system through a trap held at −64° in which SiH_3CH_2Br condensed. Repeated distillation of this fraction through a −64° trap and out of a trap held at −78° yielded pure SiH_3CH_2Br (304 mg, 2.42 mmoles, 8.4% yield based on $SiBr_4$;

TABLE 3

VAPOR PRESSURES OF SiH_3CH_2Br[a,b]

Temp. (°C)	P (mm)	
	Obsd.	Calcd.
−64.3	1.3	1.5
−57.8	2.6	2.4
−45.4	5.8	5.8
−31.8	13.7	13.8
−22.9	22.9	23.0
−18.4	29.5	29.4
0.0	74.0	74.0
2.8	84.6	84.5
11.4	123.3	123.6
1.8	80.9[c]	80.7
−10.3	45.4[c]	44.9
−196.0	0.0[c]	0.0

[a] Duration of experiment 13 h. [b] The mol.wt. of the entire sample at the conclusion of the experiment was 125.6 (calcd. 125.1). [c] Pressure observed on decreasing the temperature.

mol.wt. found 125.9, calcd. 125.1). The sample melted sharply at −91.9°. (Found: C, 9.96; H, 4.06. CH_5BrSi calcd.: C, 9.60; H, 4.03%.)

The vapor pressure of SiH_3CH_2Br was measured in an all-glass tensimeter fitted with a glass bourdon gauge which had been pre-treated for several hours with SiH_3CH_2Br. Vapor pressures at various temperatures are given in Table 3. In the range −64.3° to 11.4° they are represented by the equation: $\log P_{\text{mm}} = -1514.44/(t+273.16)+7.41383$. Additional values to those given in the Table were used in deriving the equation. The extrapolated boiling point is 60.9°, the heat of vaporization is 6.93 $\text{kcal}\cdot\text{mole}^{-1}$, and Trouton's constant is 20.7 $\text{kcal}\cdot\text{mole}^{-1}\cdot\text{deg}^{-1}$. The reproducibility of the vapor pressure curve on increasing and decreasing the temperature and the observation that the mol.wt. and IR spectrum of the sample did not change during the vapor pressure determination indicate that little, if any, thermal decomposition of the compound occurred during the experiment.

The mass spectrum of SiH_3CH_2Br was consistent with the proposed structure. Possible assignments of the major fragments ($>10\%$ relative abundance) observed are given in Table 1. A strong parent ion peak and several rearranged fragments were observed. Many of the m/e values could also be assigned in part to a different ion which contained an isotope other than that indicated. The absorption maxima, assignments, and intensities of the IR spectrum of SiH_3CH_2Br are given in Table 2. The spectrum was similar to that of SiH_3CH_2Cl given in Fig. 1.

SiH_3CH_2I

Into a 250 ml vessel containing sodium iodide (1.5 g, 10 mmoles) were distilled acetone (10 ml) and SiH_3CH_2Cl (502 mg, 6.23 mmoles; mol.wt. found 78.8, calcd. 80.6). After mild heating, sufficient to produce refluxing of acetone, for 1.5 h, the volatile material was distilled through a trap held at −96° in which SiH_3CH_2I (858 mg, 4.99 mmoles, 80.0% yield; mol.wt. found 169.4, calcd. 172.1) condensed.

TABLE 4

VAPOR PRESSURES OF $SiH_3CH_2I^{a,b}$

Temp. (°C)	P (mm)	
	Obsd.	Calcd.
−37.6	2.0	1.9
−23.1	4.7	4.7
−10.3	10.3	10.3
−2.5	15.9	15.8
5.0	22.1	22.1
13.5	35.9	35.2
17.1	41.6	41.8
23.5	58.7	58.8
17.7	43.1[c]	42.9
10.3	30.3[c]	30.3
0.1	18.2[c]	18.1
−31.3	2.8[c]	2.8
−196	0.0[c]	0.0

[a] Duration of experiment was 16 h. [b] The mol.wt. of the entire sample at the conclusion of the experiment was 172.6 (calcd. 172.1). [c] Pressure observed on decreasing the temperature.

Completely pure SiH_3CH_2I (mol.wt. found 172.0) could be obtained by slowly distilling the crude SiH_3CH_2I from a trap held at −45°. Fractions having the same vapor pressure were combined. (Found: C, 7.13; H, 3.02; I, 73.0. CH_5ISi calcd.: C, 6.98; H, 2.92; I, 73.76%.)

The vapor pressure of SiH_3CH_2I was measured in an all-glass tensimeter fitted with a glass bourdon gauge which had been pretreated for several hours with SiH_3CH_2I. Vapor pressures at various temperatures are given in Table 4. In the range −37.6° to 23.5° they are represented by the equation $\log P_{mm} = -1694.44/(t + 273.16) + 7.45829$. Additional values to those given in the Table were used in obtaining this relationship. The extrapolated boiling point is 97.0°, the heat of vaporization is 7.75 $kcal \cdot mole^{-1}$, and Trouton's constant is 21.0 $kcal \cdot mole^{-1} \cdot deg^{-1}$. The reproducibility of the vapor pressure curve on increasing and decreasing the temperature and the observation that the mol.wt. and IR spectrum of the sample did not change during the vapor pressure determination indicate that little, if any, thermal decomposition of the compound occurred during the experiment.

The mass spectrum of SiH_3CH_2I was consistent with its proposed structure. Possible assignments of the major fragments (>10% relative abundance) observed are given in Table 1. A strong parent ion peak and several rearranged fragments were observed.

The absorption maxima, assignments, and intensities of the IR spectrum of SiH_3CH_2I are given in Table 2. The spectrum was similar to that of SiH_3CH_2Cl given in Fig. 1.

Proton nuclear magnetic resonance spectra

The ^1H NMR spectra were measured by means of either a HR-60 or HA-60 Varian Associates spectrometer at 60 MHz. Compounds were measured in cyclohexane solution at approximately 5% by volume and at approximately 95% by volume. Chemical shift data were extrapolated to infinite dilution on the assumption that an approximately linear relationship between chemical shift and concentration would exist over the concentration range employed. Chemical shift and coupling constant data for SiH_3CH_2X (X=Cl, Br, I) are given in Table 5.

In order to obtain meaningful data for silicon–carbon bond shift studies, the chemical shifts of CH_3Cl, CH_3Br, and CH_3I were redetermined in this investigation under conditions identical to those used in the NMR studies of SiH_3CH_2X, *viz.*

TABLE 5

CHEMICAL SHIFT AND COUPLING CONSTANT DATA FOR SiH_3CH_2X (X=Cl, Br, I)[a]

Compound	δ(SiH_3) (ppm)	Dilution shift[b] of SiH_3 (Hz)	δ(CH_2) (ppm)	Dilution shift[b] of CH_2 (Hz)	J(H–H') (Hz)		J(^{29}Si–H) (Hz)	J(^{13}C–H) (Hz)
					Found	Calcd.		
SiH_3CH_2Cl	−2.37	−6.2	−1.50	−1.7	3.5	3.56	207.6	146.8
SiH_3CH_2Br	−2.62	−7.3	−1.14	−2.7	4.0	3.74	207.6	150.0
SiH_3CH_2I	−3.07	−8.7	−0.62	−3.8	4.0	4.00	205.8	149.0

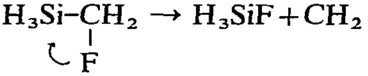
[a] Chemical shift data are given at infinite dilution with respect to cyclohexane as internal standard. A negative sign indicates a downfield shift from cyclohexane. [b] Dilution shift=δ(100% concn.)−δ(0% concn.).

in cyclohexane solvent extrapolated to infinite dilution. The chemical shift values obtained, with reference to cyclohexane, are CH_3Cl, −1.52 ppm; CH_3Br, −1.15 ppm; CH_3I, −0.60 ppm.

RESULTS AND DISCUSSION

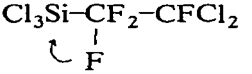
Silylmethyl chloride, SiH_3CH_2Cl, was prepared by reducing $SiCl_3CH_2Cl$ with $LiAlH_4$ as previously described[5]. The new compound SiH_3CH_2Br was synthesized in 8.6% yield from $SiBr_4$ by first converting the $SiBr_4$ to $SiBr_3CH_2Br$ with CH_2N_2 followed by reduction with $LiAlH_4$. The new compound SiH_3CH_2I was obtained in 80% yield by the metathetical reaction between SiH_3CH_2Cl and NaI in acetone.

Repeated attempts to synthesize SiH_3CH_2F from SiH_3CH_2Cl or SiH_3CH_2I and AgF or KF under a variety of different experimental conditions were unsuccessful. For example, when SiH_3CH_2I vapor was passed over solid AgF at room temperature rapid cleavage of the Si–I, Si–H and Si–C bonds resulted to give SiF_4 and CH_2F_2. It seems likely that SiH_3CH_2F may have been formed initially in these reactions, but that it then decomposed spontaneously as indicated:



$$H_3Si\text{–}\underset{F}{\underset{|}{CH_2}} \rightarrow H_3SiF + CH_2$$

This mode of decomposition is analogous to that postulated[7] for the decomposition of $SiCl_3\text{–}CF_2\text{–}CFCl_2$ to Cl_3SiF and $CFCl{=}CFCl$, the first step of which is believed to involve a transition state of the type:



$$Cl_3Si\text{–}\underset{F}{\underset{|}{CF_2}}\text{–}CFCl_2$$

The SiH_3F and CH_2 fragments formed above could then undergo additional reaction with the AgF to produce the observed products, SiF_4 and CH_2F_2. In this respect it might be noted that during the conversion of SiH_3I to SiH_3F by AgF, some fluorination of the Si–H bonds occurs and significant quantities of SiF_4 are formed[8].

No sign of thermal decomposition of silylmethyl chloride, bromide, or iodide was observed during their handling in the vacuum system, or during vapor pressure measurement experiments up to approximately room temperature. Their mass and IR spectra were consistent with their formulation as silylmethyl halides.

The proton NMR spectra of SiH_3CH_2X were analyzed as first order A_3X_2; the effective symmetries of the molecules are therefore obviously increased by rapid rotation about the Si–C bond and hence in this respect the molecules are identical to the isomeric compounds CH_3SiH_2X (X = F, Cl, Br, I).

The α-proton (methylene) chemical shifts of the SiH_3CH_2X (X = Cl, Br, I) species bear a linear relationship to the Huggins electronegativity[9] of the halogen, and they move to lower field (see Table 5) as the electronegativity of the halogen increases. In this respect they are similar to the chemical shifts found in the series CH_3X[2], SiH_3X[10], and GeH_3X[11] and to the α-proton chemical shifts in the series CH_3CH_2X[2], SiH_3SiH_2X[3], GeH_3GeH_2X[12], and CH_3SiH_2X[1] (X = Cl, Br, I). The α-proton chemical shifts of the methylsilyl halides therefore appear to be controlled primarily by the inductive effects of the halogen.

The β-proton (SiH_3) chemical shifts of the SiH_3CH_2X species, however, move in the reverse direction to that found for the α-proton chemical shifts, and they move to higher field (see Table 5) as the electronegativity of the halogen increases. In this respect they also are similar to the β-proton chemical shifts found in the series CH_3CH_2X[2], SiH_3SiH_2X[3], GeH_3GeH_2X[12], and CH_3SiH_2X[1] (X=Cl, Br, I). Thus, the chemical shifts of these protons are controlled primarily not by inductive effects but by anisotropic and related effects.

TABLE 6

DILUTION SHIFTS[a] AND BOILING POINTS OF ISOMERIC SPECIES CH_3SiH_2X AND SiH_3CH_2X

X	CH_3SiH_2X[b,c]			SiH_3CH_2X		
	SiH_2X (Hz)	CH_3 (Hz)	B.p. (°C)	CH_2X (Hz)	SiH_3 (Hz)	B.p. (°C)
Cl	−0.4	−2.5	7	−1.7	−6.2	31.7[d]
Br	−1.9	−3.9	34	−2.7	−7.3	60.9
I	−5.1	−5.5	71.8	−3.8	−8.7	97.7

[a] The negative sign indicates a downfield shift on going from a dilute to a concentrated solution. [b] NMR data (converted to 60 MHz) from ref. 1. [c] Boiling point data from ref. 15. [d] Boiling point determined in this work. Also given as 31.5° in ref. 5.

As can be seen from Table 6, the dilution shifts for both the α- and β-protons are greater in the carbon-functional SiH_3CH_2X compounds than in the corresponding silicon-functional isomers. If it is assumed that the interactions between the molecules of a given organosilicon halide are greater than those between the organosilicon halide and the solvent, cyclohexane, then the dilution shift data suggest that intermolecular interactions between SiH_3CH_2X molecules in the neat liquid are greater than those between CH_3SiH_2X molecules in the neat liquid. This is qualitatively consistent with the fact that, as shown in Table 6, the boiling point of each SiH_3CH_2X species is significantly higher than that of the corresponding isomeric CH_3SiH_2X molecule. It might also be noted that within each series of isomers the magnitude of the dilution shift increases with increasing molecular weight. This is consistent with

TABLE 7

INTERNAL CHEMICAL SHIFT DATA[a] FOR ISOMERIC CH_3SiH_2X AND SiH_3CH_2X COMPOUNDS

X	SiH_3CH_2X		CH_3SiH_2X	
	$\Delta^{X}_{\alpha\beta}$ (ppm)	$(\Delta^{X}_{\alpha\beta}-\Delta)$ (ppm[b])	$\Delta^{X}_{\alpha\beta}$ (ppm)	$(\Delta^{X}_{\alpha\beta}-\Delta)$ (ppm[b])
Cl	0.87	−2.56	4.21	0.78
Br	1.48	−1.95	3.81	0.38
I	2.45	−0.98	3.15	−0.28

[a] Internal chemical shift of $MH_3M'H_2X$ (where M or M′ is carbon or silicon) is denoted by $\Delta^{X}_{\alpha\beta}$ where $\Delta^{X}_{\alpha\beta}=|\delta(MH_3)-\delta(M'H_2X)|$. [b] $\Delta=|\delta(CH_3)-\delta(SiH_3)|$ in $CH_3SiH_3=3.43$ ppm[1]. A positive value of $(\Delta_{\alpha\beta}-\Delta)$ shows that the SiH and CH resonances in the halide derivatives are farther apart than in the parent compound, CH_3SiH_3; a negative value shows that these resonances are closer together than in the parent compound.

the fact that the total intermolecular attractive forces within a series of isomers increases with increasing molecular weight, as exemplified by the increase in boiling points on going from chloride to iodide within a given series of isomers.

The internal chemical shift, $\Delta_{\alpha\beta}^{X}$, *i.e.*, the difference in chemical shifts of the α and β resonances, of a compound $MH_3M'H_2X$, in which M and M' may be the same or different Group IV elements, is given by the expression $\Delta_{\alpha\beta}^{X} = |\delta(MH_3) - \delta(M'H_2X)|$. Internal chemical shift data have been obtained for ethyl[13], disilanyl (Si_2H_5X)[3], digermanyl (Ge_2H_5X)[12], and methylsilyl (CH_3SiH_2X)[1] halides. The corresponding data for the isomeric species CH_3SiH_2X and SiH_3CH_2X are given in Table 7. In ethyl, disilanyl, digermanyl, and methylsilyl halides, the internal chemical shift, $\Delta_{\alpha\beta}^{X}$, decreases on proceeding from the fluoride to the iodide. However, in the series SiH_3CH_2X, $\Delta_{\alpha\beta}^{X}$, *increases* on proceeding from the chloride to iodide. This reverse trend can be explained on examination of the data given in Table 8 which show the extent to which a given proton resonance (either CH_3 or SiH_3) in CH_3SiH_3 is shifted when a proton is replaced by a halogen. All protons move downfield, but for any given substituent, X, in a given compound, the β chemical shifts are modified to a much smaller extent than the α chemical shifts. Hence, trends in the internal chemical shift values are determined chiefly by the inductively-controlled chemical shifts of the α-protons. In SiH_3CH_2X species, the CH_2X resonance falls to high field of the SiH_3 resonance, and hence as the electronegativity of X is decreased the CH_2X resonance moves even farther upfield (the SiH_3 resonance remaining essentially constant), and $\Delta_{\alpha\beta}^{X}$ therefore increases. In the CH_3SiH_2X compounds the SiH_2X resonance is to low field of the CH_3 resonance, and hence it moves closer (smaller $\Delta_{\alpha\beta}^{X}$) to the CH_3 resonance as the electronegativity of X decreases.

TABLE 8

MODIFICATION OF CHEMICAL SHIFTS IN CH_3SiH_3 UPON REPLACEMENT OF A HYDROGEN BY A HALOGEN[a]

X	α-Protons (ppm)		β-Protons (ppm)	
	$\delta(Si\text{–}CH_2\text{–}X) - 1.32$	$\delta(C\text{–}SiH_2\text{–}X) - (-2.11)$	$\delta(H_3Si\text{–}C\text{–}X) - (-2.11)$	$\delta(H_3C\text{–}Si\text{–}X) - 1.32$
Cl	−2.81	−1.17	−0.39	−0.25
Br	−2.46	−0.94	−0.56	−0.51
I	−1.94	−0.53	−0.81	−0.96

[a] In CH_3SiH_3 the chemical shift of the SiH protons is −2.11 ppm downfield from cyclohexane, and the chemical shift of the CH protons is 1.32 ppm upfield from cyclohexane at infinite dilution[1].

If the internal chemical shifts, $\Delta_{\alpha\beta}^{X}$, for SiH_3CH_2X and CH_3SiH_2X species are "corrected" for the internal chemical shift in the parent compound, CH_3SiH_3, then it can be seen from Table 7 that these "corrected" values of the internal chemical shifts, the quantity $\Delta_{\alpha\beta}^{X} - \Delta$, decrease in both series as the electronegativity of the halogen decreases.

Catenation shifts, *e.g.*, a carbon–carbon bond shift[2], Δ_{C-C}^{X}, a silicon–silicon bond shift[3], Δ_{Si-Si}^{X}, and a germanium–germanium bond shift[12], Δ_{Ge-Ge}^{X}, have previously been found on examining the proton spectra of analogous pairs of MH_3X and MH_3MH_2X (M = C, Si or Ge) compounds having an identical substituent, X. The above types of shift are defined by the relationship

$$\Delta^{X}_{M-M} = [\delta(MH_3) \text{ in } MH_3X] - [\delta(MH_2) \text{ in } MH_3MH_2X]$$

and they therefore show the change in chemical shift of the MH_3 protons in MH_3X when, in a hypothetical process, one of the protons is "replaced" by a MH_3 group to give the corresponding MH_3MH_2X compound. With the exception of the iodide in the SiH_3I/SiH_3SiH_2I and GeH_3I/GeH_3GeH_2I systems, the replacement of a hydrogen in MH_3X by a MH_3 group causes a downfield shift of the α-protons. A somewhat similar phenomenon, *i.e.*, a carbon–silicon bond shift, Δ^{X}_{C-Si}, has been observed in the pairs of compounds SiH_3X/CH_3SiH_2X. The values are $\Delta^{Cl}_{C-Si}=0.13$ ppm, $\Delta^{Br}_{C-Si}=0.32$ ppm, and $\Delta^{I}_{C-Si}=0.59$ ppm.

It was interesting to note in the present study that the "replacement" of a hydrogen in CH_3X by a SiH_3 group brought about a barely discernable change in chemical shift of the remaining CH protons, but a silicon–carbon bond shift, Δ^{X}_{Si-C}, could definitely be identified. The values obtained are $\Delta^{Cl}_{Si-C}=-0.03$ ppm, $\Delta^{Br}_{Si-C}=-0.01$ ppm, and $\Delta^{I}_{Si-C}=+0.02$ ppm. Although the absolute magnitude of the silicon–carbon bond shifts are strikingly small, the spread of 0.05 ppm from the chloride to the iodide is well outside the range of experimental error.

It has been noted[1] that the vicinal coupling constant $J(H-H')$ in CH_3SiH_2X compounds is related to within 0.3 Hz to the electronegativities of the substituent X by the empirical relationship

$$J(H-H') = 4.4 \cdot [1.0 - 0.2 \cdot (\chi_X - \chi_H)]$$

in which χ_X and χ_H are the Huggins electronegativities of the substituent X and hydrogen, respectively. As can be seen from Table 5, the same relationship also holds remarkably well for the SiH_3CH_2X compounds. Certain relationships involving the $^{29}Si-H$ and $^{13}C-H$ coupling constants have been noted in an earlier publication[14].

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REFERENCES

1 E. A. V. Ebsworth and S. G. Frankiss, *Trans. Faraday Soc.*, 59 (1963) 1518.
2 J. R. Cavanaugh and B. P. Dailey, *J. Chem. Phys.*, 34 (1961) 1099.
3 C. H. Van Dyke and A. G. MacDiarmid, *Inorg. Chem.*, 3 (1964) 1071.
4 L. G. L. Ward and A. G. MacDiarmid, *J. Amer. Chem. Soc.*, 82 (1960) 2151; *J. Inorg. Nucl. Chem.*, 21 (1962) 287; 20 (1961) 345; A. D. Craig, J. V. Urenovitch and A. G. MacDiarmid, *J. Chem. Soc.*, (1962) 548.
5 H. D. Kaesz and F. G. A. Stone, *J. Chem. Soc.*, (1957) 1433.
6 A. Ya. Yakubovitch and V. A. Ginsburg, *Zh. Obshch. Khim.*, 22 (1952) 1783.
7 R. N. Haszeldine and J. C. Young, *J. Chem. Soc.*, (1960) 4503.
8 H. J. Emeléus and A. G. Maddock, *J. Chem. Soc.*, (1946) 1131.
9 M. L. Huggins, *J. Amer. Chem. Soc.*, 75 (1953) 4123.
10 E. A. V. Ebsworth and J. J. Turner, *J. Phys. Chem.*, 67 (1963) 805.
11 E. A. V. Ebsworth, S. G. Frankiss and A. G. Robiette, *J. Mol. Spectrosc.*, 12 (1964) 299.
12 E. J. Spanier and A. G. MacDiarmid, *J. Inorg. Nucl. Chem.*, in press.
13 B. P. Dailey and J. N. Schoolery, *J. Amer. Chem. Soc.*, 77 (1955) 3977.
14 T. Yoshioka and A. G. MacDiarmid, *J. Mol. Spectrosc.*, 21 (1966) 103.
15 C. Eaborn, *Organosilicon Compounds*, Butterworths, London, 1960, p. 188–189.