the shifts obtained in $ClCH_2OCH_3$ (τ_{CH_2} 4.7; τ_{CH_3} 6.62). Anomalous chemical shifts have been previously noted for the H(Si) chemical shifts of silane derivatives that contain two or more electronegative substituents such as those containing oxygen or fluorine attached to silicon.[31] Actually, the chemical shift of the SiH_2 protons of $SiH_2(OSiH_3)F$ is not that surprising, considering that it is just about the average of the SiH_2 chemical shifts found for the related compounds $SiH_2(OSiH_3)_2$ (τ 5.46) and SiH_2F_2(τ 5.29).[31,32]

It was not possible to fluorinate the silicon–hydrogen bonds of the alkoxysilane CH_3OSiH_3 or the bis(disilanyl) ether $(SiH_3SiH_2)_2O$ by using PF_5. In both cases, cleavage of the silicon–oxygen bond occurred. We

$$CH_3OSiH_3 + PF_5 \longrightarrow SiH_3F + CH_3OPF_4$$

$$(SiH_3SiH_2)_2O + PF_5 \longrightarrow 2SiH_3SiH_2F + POF_3$$

were able to isolate and characterize the SiH_3F produced in the reaction of CH_3OSiH_3 with PF_5, but it was not possible to characterize definitely the CH_3OPF_4 presumably produced. The latter compound is known to be very reactive and easily decomposes even at low temperatures.[33] We did detect the presence of CH_3OPOF_2 in the reaction. This is reported to be one of the decomposition products of CH_3OPF_4.[33] The interaction of phosphorus pentafluoride with $CH_3OSi(CH_3)_3$ likewise produced $(CH_3)_3SiF$ and an unstable compound again presumed to be CH_3OPF_4, based on the presence of CH_3OPOF_2 in the reaction products.

The cleavage of the silicon–oxygen bond of siloxanes and alkoxysilanes by Lewis acids is thought to proceed *via* the initial formation of an acid–base adduct.[34,35] Noting that the silicon–hydrogen bond of organosilanes such as $C_2H_5SiH_3$ can be fluorinated by PF_5,[1b,29] it can be assumed that the fluorination reaction is not particularly dependent on the basicity of the silicon compound. Thus, owing to the greater basicity of CH_3OSiH_3 relative to $(SiH_3)_2O$,[10,36] there would be a greater tendency for the alkoxysilane to undergo adduct formation and hence cleavage with PF_5 rather than for $(SiH_3)_2O$ to undergo reaction in this manner. The reaction rates are apparently different enough to favor the cleavage in CH_3OSiH_3, rather than the fluorination of the silicon–hydrogen bond. In the $(SiH_3)_2O$–PF_5 reaction, both the cleavage and the fluorination reactions are observed to take place.

It has previously been shown that the silicon–oxygen bond in $(SiH_3SiH_2)_2O$ is cleaved more readily by boron trichloride than the same bond in $(SiH_3)_2O$.[37] Thus, PF_5 may also have a greater tendency to cleave the silicon–oxygen bond of $(SiH_3SiH_2)_2O$ than of $(SiH_3)_2O$. If this is true, the difference is apparently enough to favor completely the cleavage over the fluorination in the case of the $(SiH_3SiH_2)_2O$ reaction. No partially fluorinated bis(disilanyl) ethers were detected in the reaction of $(SiH_3SiH_2)_2O$ with phosphorus pentafluoride at −78°.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE-MELLON UNIVERSITY,
PITTSBURGH, PENNSYLVANIA 15213

The Preparation and Characterization of Silylgermylmethane and Some of Its Inorganic Derivatives[1]

BY CHARLES H. VAN DYKE,* EDWARD W. KIFER, AND GERST A. GIBBON

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Silylgermylmethane, $GeH_3CH_2SiH_3$, prepared by the interaction of SiH_3CH_2Cl with $NaGeH_3$, reacts with hydrogen chloride in the presence of aluminum chloride to yield $GeH_3CH_2SiH_2Cl$, $GeH_3CH_2SiHCl_2$, and $(SiH_3CH_2)_2GeH_2$. The hydrolysis of $GeH_3CH_2SiH_2Cl$ or its treatment with mercuric oxide leads to the formation of $(GeH_3CH_2SiH_2)_2O$. The new mixed hydride derivatives have been isolated and characterized. Their infrared and proton nmr spectra are discussed.

Although properties of the silicon–hydrogen and germanium–hydrogen bonds have been reasonably well established by studies of individual silanes and germanes, very little is known about the chemistry of compounds that have both these bonds present in the same molecule. The chemical properties of silanes and germanes are similar in many respects[2,3] and a general study of mixed silicon–germanium hydrides should help to point out important differences which may not be completely apparent in studies of individual compounds containing one or the other of

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these bonds. The parent mixed hydride GeH_3SiH_3 is known,[4] but its chemistry is very limited, owing to the instability of the silicon–germanium bond.[5] In order to obtain information about the properties of the silicon–hydrogen and germanium–hydrogen bonds when they are present in the same molecule, we chose to study the mixed hydride $GeH_3CH_2SiH_3$ and some of its inorganic derivatives.[6]

Experimental Section

Apparatus.—A conventional Pyrex-glass high-vacuum system was used to manipulate all volatile compounds.[7] Stopcocks and ground-glass joints were lubricated with Apiezon N grease. Mass spectra were obtained by means of a CEC-103C mass spectrometer or, for $(SiH_3CH_2)_2GeH_2$ and $(GeH_3CH_2SiH_2)_2O$, an AEI-MS-9 mass spectrometer. The spectra were complex owing to the presence of five naturally occurring isotopes of germanium in significant natural abundance. Special care had to be taken to exclude all traces of moisture from the spectrometer in order to obtain satisfactory spectra for the compounds that contained silicon–chlorine bonds. Infrared spectra were obtained on a Perkin-Elmer Model 457 spectrophotometer with the sample confined in a 10-cm cell fitted with KBr windows. Proton nmr spectra were obtained on a Varian A-60 or a Hitachi Perkin-Elmer R20 spectrometer operating at ambient temperatures. Gas chromatographic separations were performed on a modified Varian Aerograph Model A-90-P3 gas chromatograph equipped with a special inlet and collection system that allowed the samples to be chromatographed without exposure to air.[8] The unit was operated at a flow rate of 100 cm^3 of He min^{-1} and at a column temperature of 30°. Melting points were obtained by the Stock magnetic plunger method.[9]

Materials.—$ClCH_2SiH_3$ was prepared by the reduction of $ClCH_2SiCl_3$ with $LiAlH_4$ in di-*n*-butyl ether.[10] The compound condenses in a trap at −96° and was shown to be pure by gas chromatography. GeH_4, purity confirmed by gas chromatography and by the compound's molecular weight (calcd 76.6, found 76.6) and infrared spectrum,[11] was prepared by the reduction of GeO_2 with $NaBH_4$.[12] $NaGeH_3$ was prepared by the reaction of GeH_4 with sodium in liquid ammonia.[13] Removal of the ammonia solvent *in vacuo* afforded solid $NaGeH_3$. All other reagents used are commercially available.

Syntheses. $GeH_3CH_2SiH_3$.—$ClCH_2SiH_3$ (10.2 mmol) was distilled into a 250-ml flask containing approximately 10 mmol of freshly prepared $NaGeH_3$. The system was allowed to react for 15 min at room temperature. Distillation of the products in the vacuum line produced $GeH_3CH_2SiH_3$ (3.63 mmol, 35% yield) as a condensate in a −112° trap. The gas-phase molecular weight of the compound was 121.0 (calcd for $GeH_3CH_2SiH_3$ 120.7). It melted sharply at −134.8° and showed a single peak in its gas chromatogram (0.25 in. × 15 ft copper column, 20% squalane on Chromosorb W, retention time 15.3 min). The mass spectrum of the compound at 70 eV showed a low-intensity fragment for the parent ion and other expected fragments at lower mass units.

$GeH_3CH_2SiH_2Cl$.—Freshly purified $GeH_3CH_2SiH_3$ (5.0 mmol) and anhydrous HCl (2.0 mmol) were condensed into a 1-l. bulb that contained about 0.5 g of aluminum chloride sublimed on its walls. The gaseous mixture was held at room temperature for 24 hr. The contents of the flask were then slowly distilled through several traps at −196° to remove the hydrogen formed. The condensable materials were distilled through a −134° trap to remove GeH_4 (2.8 mmol recovered) formed. The unreacted $GeH_3CH_2SiH_3$ was removed by its distillation through a trap at −78°. Crude $GeH_3CH_2SiH_2Cl$ (mol wt 157.3, calcd 155.2) that condensed in the −78° trap was further purified by allowing it to distil slowly through a −78° trap with pumping. The pure compound (1.3 mmol, 65% yield) had a gas-phase molecular weight of 155.7 and showed the expected mass spectral fragmentation pattern. It melted sharply at −129.2°.

The compound could be recovered from the gas chromatography unit (single peak noted) providing the carrier gas and the various parts of the chromatograph in which the sample was in contact were dry. The carrier gas was passed through a drying tube and through a coil immersed in a dewar flask of liquid nitrogen. A sample of $GeH_3CH_2SiH_2Cl$ had a retention time of 2.1 min, when a 0.25 in. diameter × 5 ft glass column packed with a 20% w/w column of benzyl ether on Chromosorb W was used.

$GeH_3CH_2SiHCl_2$.—$GeH_3CH_2SiH_3$ (2.5 mmol) and anhydrous HCl (2.0 mmol) were condensed into a 1-l. bulb that contained freshly sublimed aluminum chloride and were allowed to react at room temperature in the gas phase for 12 hr. Hydrogen was removed from the products by its distillation through several traps at −196°. GeH_4 was removed by its distillation through a −134° trap. The condensate at −134° contained $GeH_3CH_2SiH_3$, $GeH_3CH_2SiH_2Cl$, $GeH_3CH_2SiHCl_2$, and some $(SiH_3CH_2)_2GeH_2$. $GeH_3CH_2SiHCl_2$ (0.73 mmol, 36% yield, mol wt 188.6, calcd 189.6) was separated from the product mixture by its condensation in a −64° trap. The compound showed the expected mass spectral fragmentation pattern and a single peak in its gas chromatogram at 7.8 min using the column and conditions described for $GeH_3CH_2SiH_2Cl$.

$(GeH_3CH_2SiH_2)_2O$.—$GeH_3CH_2SiH_2Cl$ (2.0 mmol) was allowed to react with about 2 g of water in a 100-ml bulb for 15 min at room temperature. The products were distilled through a −23° bath and then through a −64° bath. The $(GeH_3CH_2SiH_2)_2O$ (0.9 mmol, 90% yield) condensed in the −64° bath and was further dried by passing it over solid "Drierite." The purified compound had a molecular weight of 253.8 (calcd 255.5). This compound was also conveniently prepared by passing $GeH_3CH_2SiH_2Cl$ (1.0 mmol) through a HgO–sand mixture. Four passes were required for the conversion. The product (0.31 mmol, 60% yield, mol wt 254.4) was purified by its condensation in a −64° bath. The compound showed the expected mass spectral fragmentation pattern. Precise mass measurements on two peaks in the high-mass region yielded the following results (ion, measured mass, calculated mass): $C_2H_{11}OSi_2{}^{72}Ge_2{}^+$, 250.8790, 250.8790; $C_2H_{13}OSi_2{}^{72}Ge^+$, 256.8930, 256.8928.

$(SiH_3CH_2)_2GeH_2$.—Small amounts of this compound were detected in the products of each of the reactions of $GeH_3CH_2SiH_3$ with hydrogen chloride in the presence of aluminum chloride. After allowing the products to distil through a −78° trap to remove the $GeH_3CH_2SiH_2Cl$ and unreacted $GeH_3CH_2SiH_3$, the condensate was then redistilled through a −64° bath. The pure $(SiH_3CH_2)_2GeH_2$ (mol wt: calcd, 164.9; found, 165.1) is volatile at this temperature and collects in the terminal −196° bath. Variable amounts of this compound formed in each of the reactions investigated and it was noted in at least one experiment that the reaction produced an almost equivalent amount of GeH_4. The mass spectral fragmentation pattern of $(SiH_3CH_2)_2GeH_2$ is consistent with its formulation. Precise mass measurements, taken on several fragments, yielded the following data (ion, measured mass, calculated mass): ${}^{74}Ge{}^{28}Si{}^{12}CH_4{}^+$, 117.9294, 117.9294; ${}^{72}Ge{}^{28}Si{}^{12}CH_6{}^+$, 117.9459, 117.9460; ${}^{72}Ge{}^{28}Si_2{}^{12}C_2H_{11}{}^+$, 162.9619, 162.9620.

Vapor Pressures.—The vapor pressures of purified samples of $GeH_3CH_2SiH_3$ and $GeH_3CH_2SiH_2Cl$ were determined at a number of temperatures and are listed in Tables I and II. The data were obtained in a glass–mercury manometer system, the inner

TABLE I

REPRESENTATIVE VAPOR PRESSURES OF $GeH_3CH_2SiH_3$

Temp, °C	*P*, Torr		Temp, °C	*P*, Torr	
	Calcd	Obsd		Calcd	Obsd
−64.0	3.9	3.8	−36.6[a]	28.0	28.2
−50.0	11.3	11.5	−45.3[a]	15.8	15.6
−45.8	15.2	15.5	−64.0[a]	3.9	3.9
−44.3	16.9	16.9			
−36.4	28.4	28.3			
−31.2	39.2	38.5			

[a] Pressure observed on decreasing the temperature.

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TABLE II
REPRESENTATIVE VAPOR PRESSURES OF $GeH_3CH_2SiH_2Cl$

Temp, °C	*P*, Torr		Temp, °C	*P*, Torr	
	Calcd	Obsd		Calcd	Obsd
−14.8	10.4	10.5	12.3	37.8	38.2
−11.4	12.4	12.3	15.4	43.2	43.0
−4.6	17.4	17.4	4.0[a]	26.2	26.2
0.0	21.7	21.7	−10.7[a]	12.9	12.9
5.5	28.0	28.3	−22.9[a]	6.7	6.9
10.3	34.7	34.2	−196[a]	...	0

[a] Pressure observed on decreasing the temperature.

surface of which had been exposed to separate samples of the compounds for 12 hr. The infrared spectra of the samples at the conclusion of the vapor pressure measurements were identical with the spectra of the pure compounds.

Vapor pressures in the ranges studied are given by the following equations: For $GeH_3CH_2SiH_3$

$$\log P_{\text{Torr}} = \frac{-1545.7}{t + 273.16} + 7.9811$$

and for $GeH_3CH_2SiH_2Cl$

$$\log P_{\text{Torr}} = \frac{-1526.2}{t + 273.16} + 6.9243$$

Extrapolated boiling points are 29.9° for $GeH_3CH_2SiH_3$ and 104.3° for $GeH_3CH_2SiH_2Cl$.

The vapor pressures of the remaining new compounds prepared were only measured at 0° owing to their low volatility. The data, useful for checking the purity of the compounds, are as follows (compound, vapor pressure at 0°): $GeH_3CH_2SiHCl_2$, 3.7 Torr; $(GeH_3CH_2SiH_2)_2O$, 7.6 Torr; $(SiH_3CH_2)_2GeH_2$, 8.6 Torr.

Infrared Spectra.—Major absorptions noted in the gas-phase infrared spectra of $GeH_3CH_2SiH_3$, $GeH_3CH_2SiH_2Cl$, $GeH_3CH_2SiHCl_2$, $(GeH_3CH_2SiH_2)_2O$, and $(SiH_3CH_2)_2GeH_2$ are listed as follows (cm^{-1}). $GeH_3CH_2SiH_3$: 2955, 2920 (d, vw), 2153 (s), 2080 (s), 1368 (vw), 1048 (m), 941 (vs), 880 (vw), 850 (s), 840 (sh), 775 (sh), 752 (m), 745 (sh), 720 (m), 710 (sh), 540 (vw, br), ~475 (vw, br). $GeH_3CH_2SiH_2Cl$: 2954, 2915 (d, vw), 2180 (s), 2088 (s), 1362 (w), 1051 (m), 1008 (w), 955 (m), 880, 870 (d, vs), 841 (vs), 758 (s), 736 (m), 673 (w), 647 (w), 544 (w), 510, 502 (d, vw), 483 (w). $GeH_3CH_2SiHCl_2$: 2942, 2910 (d, vw), 2210 (s), 2095 (s), 1382, 1365 (d, w), 1055 (m), 1005 (w), 960 (vw), 863 (m), 812 (vs), 762 (s), 701, 694 (d, w), 672 (w), 630 (w), 570 (m), 480 (w). $(GeH_3CH_2SiH_2)_2O$: 2950 (vw), 2150 (s), 2080 (s), 1380, 1363 (d, w), 1083 (s), 1050 (m), 1009 (w), 967 (m), 925 (vw), 894 (s), 841 (vs), 774 (w), 742 (m), 650 (w). $(SiH_3CH_2)_2GeH_2$: 2942, 2910 (d, vw), 2160 (s), 2056 (s), 1380 (vw), 1055, 1049 (d, m), 940 (vs), 885, 876 (d, w), 805 (m), 750 (m), 718 (m), 662 (w).

Results and Discussion

Syntheses and Reactions.—For stability purposes, the mixed hydride chosen for investigating the chemistry of compounds that contain both silicon–hydrogen and germanium–hydrogen bonds was $GeH_3CH_2SiH_3$. The compound was prepared in a 35% yield by the interaction of SiH_3CH_2Cl with $NaGeH_3$: $SiH_3CH_2Cl + GeH_3Na \rightarrow GeH_3CH_2SiH_3 + NaCl$. Pure $GeH_3CH_2SiH_3$ could be manipulated in normal vacuum-line operations without any apparent decomposition.

Individual organosilanes and organogermanes react in the gas phase with hydrogen chloride in the presence of aluminum chloride to form organochlorosilanes and organochlorogermanes, respectively.[14-16] An exact comparison of the minimum temperatures required for reaction in each of these systems has not been reported, although the CH_3GeH_3 halogenation is reported to occur at room temperature,[14,15] whereas the satisfactory halogenation of CH_3SiH_3 requires temperatures of about 100°.[16] In each case the formation of some of the dihalo product is also observed. We have found that the interaction of the mixed hydride $GeH_3CH_2SiH_3$ with hydrogen chloride in the presence of aluminum chloride at room temperature leads to predominant substitution on the silicon, rather than the germanium. This is somewhat unexpected, based on the reported reaction conditions for the analogous CH_3SiH_3 and CH_3GeH_3 reactions.[14-16] Employing a 5:2 mole ratio of $GeH_3CH_2SiH_3$ to hydrogen chloride in the reaction, $GeH_3CH_2SiH_2Cl$ could be isolated in a 65% yield. In order to introduce more than one chlorine into $GeH_3CH_2SiH_3$, a reaction was carried out with a 5:4 mole ratio of $GeH_3CH_2SiH_3$ to hydrogen chloride. In this case the predominant formation of $GeH_3CH_2SiHCl_2$ (36% yield) was noted, rather than the formation of any germanium-substituted compound.

It was of particular interest to note that the mixed hydride $(SiH_3CH_2)_2GeH_2$ was produced in small amounts in the above chlorination reactions. The observation that $GeH_3CH_2SiH_3$ alone in the presence of aluminum chloride did not decompose to give this product led us to consider the possbility that chlorine substitution did occur to some extent on the germanium, which was then followed by a disproportionation of the type $2SiH_3CH_2GeH_2Cl \rightarrow GeH_2Cl_2 + (SiH_3CH_2)_2GeH_2$. However, we were not able to detect the formation of any GeH_2Cl_2 in the reaction. This compound has a very characteristic infrared absorption spectrum[17-19] and should have been easily detected if it were present. Germane was definitely produced in these reactions and we thus conclude that in the presence of aluminum chloride and hydrogen chloride, $GeH_3CH_2SiH_3$ undergoes disproportionation according to $2GeH_3CH_2SiH_3 \rightarrow GeH_4 + (SiH_3CH_2)_2GeH_2$.

Proton Nmr Spectra.—The proton nmr spectrum of the compounds prepared in this work could be analyzed on the basis of first-order couplings. The spectrum of $GeH_3CH_2SiH_3$, shown on a low-scale expansion in Figure 1, consists of a 1:6:15:20:15:6:1 septet assigned to the CH_2 proton resonance and a 1:3:3:1 quartet that is actually a combination two 1:2:1 triplets assigned to the GeH_3 and SiH_3 proton resonances. The observed quartet results from the nearly identical $\overline{\mathrm{H(Si)H}}\mathrm{(C)}$ and $\overline{\mathrm{H(Ge)H}}\mathrm{(C)}$ coupling constants and the difference between the Si–H and Ge–H chemical shifts being about the same order of magnitude as the H–H coupling. There are two low-intensity triplet ^{29}Si ($I = {}^1/_2$, 5% abundant) satellites centered about the low-field triplet of the combined triplets thus establishing the unambiguous assignment of the Si–H protons. On further scale expansion, additional splittings of the Si–H and Ge–H resonances were observed as a result of long-range H–H coupling. As expected, the C–H resonance was found to consist of a quartet of quartets as shown in Figure 2 on further scale expansion. The analysis of the spectra for the derivatives of GeH_3-

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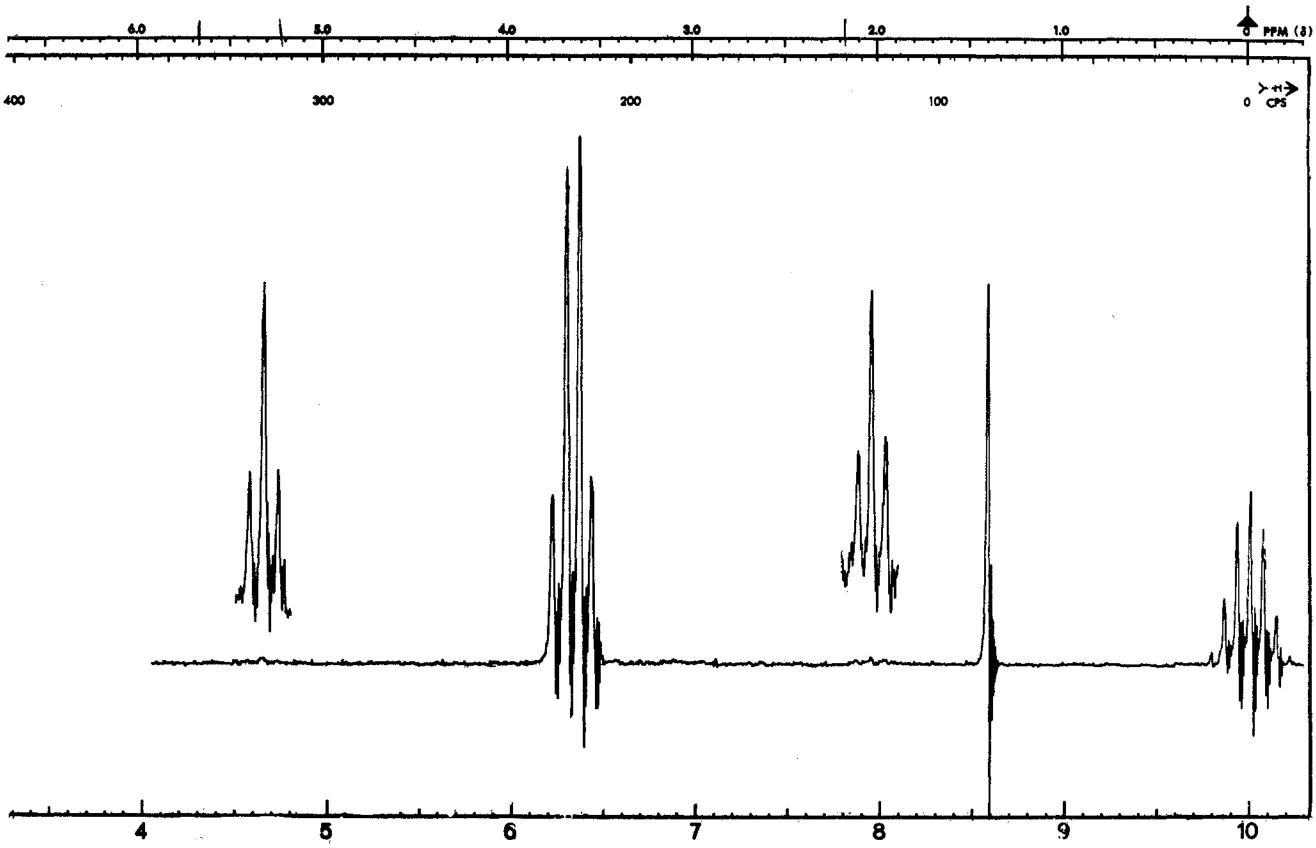

Figure 1.—Proton nuclear magnetic resonance spectrum of $GeH_3CH_2SiH_3$ (500-cps sweep width).

CH_2SiH_3 could be made in a similar manner. Chemical shifts and coupling constants for the new compounds are summarized in Table III.

TABLE III
PROTON NUCLEAR MAGNETIC RESONANCE DATA FOR $GeH_3CH_2SiH_3$ AND ITS DERIVATIVES[a,b]

Compound	τ_{SiH}	τ_{GeH}	τ_{CH}	J_{CH-GeH}	J_{CH-SiH}	$J_{^{29}Si-H}$
$GeH_3CH_2SiH_3$	6.29	6.37	10.01	4.0	4.5	198.7
$GeH_3CH_2SiH_2Cl$	5.22	6.35	9.60	3.9	3.9	234.3
$GeH_3CH_2SiHCl_2$	4.47	6.30	9.36	3.9	1.9	285.0
$(GeH_3CH_2SiH_2)_2O$	5.23	6.36	9.62	3.8	3.6	...
$SiH_3CH_2GeH_2CH_2SiH_3$	6.02	6.31	9.98	3.7	4.6	...

[a] Cyclohexane was used as solvent and internal standard ($\tau_{C_6H_{12}}$ 8.56) in all cases except for $(GeH_3CH_2SiH_2)_2O$. Concentrations were approximately 10–20% by volume. The spectrum of $(GeH_3CH_2SiH_2)_2O$ was determined in $CFCl_3$ (10% by volume) with a small amount of $HCCl_3$ added as internal reference (τ_{HCCl_3} 2.73). [b] Coupling constants are reported in hertz.

The replacement of one or two hydrogen atoms on silicon by an electronegative substituent in $GeH_3CH_2SiH_3$ produces the same general effect on the nmr parameters as does the analogous replacements in SiH_4[20] or CH_3SiH_3.[21,22] For example, the chemical shift of the Si–H protons moves to low fields and the ^{29}Si–H coupling constant shows a significant increase with increasing chlorine substitution. The actual values for $GeH_3CH_2SiH_2Cl$ and $GeH_3CH_2SiHCl_2$ are very close to the values found in cyclohexane solutions of CH_3SiH_2Cl (τ_{SiH} 5.28, $J_{^{29}SiH}$ = 229.0 Hz) and CH_3SiHCl_2 (τ_{SiH} 4.48, $J_{^{29}SiH}$ = 280.8 Hz), respectively.[21,22] This indicates that the substitution of a hydrogen bound to carbon by a GeH_3 grouping in halogen derivatives of CH_3SiH_3 has little effect on the chemical shifts and coupling constants of the Si–H protons. The significant decrease in the $\overline{\mathrm{H(C)H}}\mathrm{(Si)}$ coupling with increasing chlorine substitution on silicon also parallels the $\overline{\mathrm{H(C)H}}\mathrm{(Si)}$ coupling constant trend noted in CH_3SiH_3, CH_3SiH_2Cl, and CH_3SiHCl_2.[21,22] The magnitude of the vicinal H–H coupling constant for these compounds can also be predicted by the empirical equations derived by Ebsworth and Frankiss for CH_3SiH_2X and CH_3SiHXY type compounds.[21,22] Nmr data for $(GeH_3CH_2SiH_2)_2O$ were obtained in $CFCl_3$ owing to solubility problems and strictly speaking should not be compared with known data for $(CH_3SiH_2)_2O$ in cyclohexane.[22]

Infrared Data.—Most of the absorptions observed in the infrared spectra of $GeH_3CH_2SiH_3$ and its inorganic derivatives can be tentatively assigned from the detailed assignments previously given for CH_3GeH_3,[23] $(SiH_3)_2CH_2$,[24] CH_3SiH_2Cl,[25] and $(CH_3SiH_2)_2O$.[25] The C–H stretches appear in the 2900-cm^{-1} region while the Si–H stretches and the Ge–H stretches are in the 2150–2210- and 2056–2095-cm^{-1} regions, respectively. The CH_2 deformations appear in the 1362–1382-cm^{-1} (scissors) and 1049–1055-cm^{-1} (wagging) regions. The SiH_3 deformation modes are at 948 cm^{-1} for $GeH_3CH_2SiH_3$ and at 940 cm^{-1} for $(SiH_3CH_2)_2GeH_2$. The

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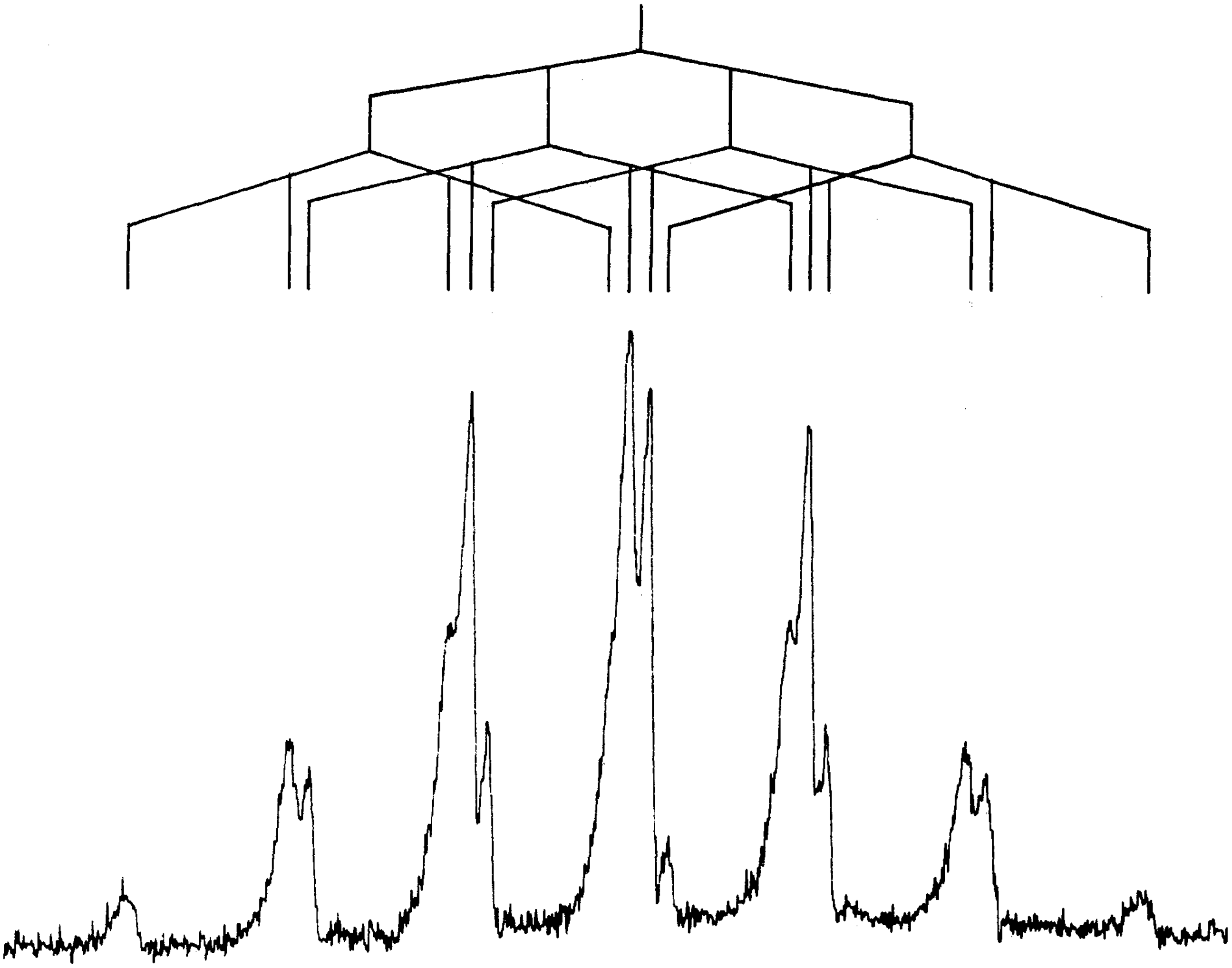

Figure 2.—Proton nuclear magnetic resonance spectrum of the CH_2 protons of $GeH_3CH_2SiH_3$ (50-cps sweep width).

SiH and SiH_2 bending modes of the derivatives are in the 955–967-cm^{-1} region. The Si–C stretches are in the 750–774-cm^{-1} region while the Ge–C stretches are most likely those absorptions in the 650-cm^{-1} region. Silicon–chlorine stretches are at 544 cm^{-1} for $GeH_3CH_2SiH_2Cl$ and at 570 cm^{-1} for $GeH_3CH_2SiHCl_2$. The asymmetric silicon–oxygen stretch of $(GeH_3CH_2SiH_2)_2O$ is the band at 1083 cm^{-1}.

The shift in the Si–H stretches toward higher frequencies with increasing chlorine substitution in the series $GeH_3CH_2SiH_3$ (2153 cm^{-1}), $GeH_3CH_2SiH_2Cl$ (2180 cm^{-1}), and $GeH_3CH_2SiHCl_2$ (2210 cm^{-1}) is predicted on the basis of electronegativity considerations.[26] The Ge–H stretching frequency also increases with increasing chlorine substitution in the series (2080, 2088, and 2095 cm^{-1}, respectively). The fact that the Si–H frequency of $(GeH_3CH_2SiH_2)_2O$ (2150 cm^{-1}) is shifted only slightly from that of $GeH_3CH_2SiH_3$ (2153 cm^{-1}) is in accord with Smith and Angelotti's conclusion that the Si–H absorption is not greatly affected by the presence of a single adjacent oxygen.[26]

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