TABLE V

NMR DATA FOR BIS-AMINE $BH_2^+PF_6^-$ SALTS

Amine	CH_3 δ, ppm	Aromatic protons δ, ppm (J, cps)	M[a]	^{11}B resonance
$(2\text{-pic})_2BH_2^+PF_6^-$	2.68	$H_{3,5}$, 7.77	m	22.3 ± 1.1, J = 90 cps
		$H_{4,6}$, 8.27	m	
$(3\text{-pic})_2BH_2^+PF_6^-$	2.55	H_5, 7.80	Q	23.1 ± 0.8 b
		H_4, 8.18 (8)	D	
		$H_{2,6}$, 8.57	bD	
$(4\text{-pic})_2BH_2^+PF_6^-$	2.58	$H_{2,6}$, 8.53 (6)	D	19.2 ± 1.1 b
		$H_{3,5}$, 7.67 (6)	D	
$(2,3\text{-lut})_2BH_2^+PF_6^-$	2-CH_3, 2.63	H_5, 7.60 (6)	T	20.0 ± 0.5
	3-CH_3, 2.53	$H_{4,6}$, 8.20 (6)	D	
$(2,4\text{-lut})_2BH_2^+PF_6^-$	2-CH_3, 2.62	$H_{3,5}$, 7.50 (6)	D	22.0 ± 0.8, J = 90 cps
	4-CH_3, 2.57	H_6, 8.10 (6)	D	
$(2,5\text{-lut})_2BH_2^+PF_6^-$	2-CH_3, 2.62	H_3, 7.63 (8)	D	22.0 ± 0.8, J = 90 cps
	5-CH_3, 2.45	$H_{4,6}$, 8.00	b	
$(2,6\text{-lut})_2BH_2^+PF_6^-$ [b]	2,6-CH_3, 1.88	$H_{3,5}$, 6.93 (8)	D	26.6 ± 1, J = 110 cps
		H_4, 7.46	m	
$(3,4\text{-lut})_2BH_2^+PF_6^-$	3-CH_3, 2.43	H_5, 7.62 (6)	D	18.9 ± 0.8 b
	4-CH_3, 2.50	$H_{2,6}$, 8.4	b	
$(3,5\text{-lut})_2BH_2^+PF_6^-$	3,5-CH_3, 2.50	H_4, 7.97	bS	20 ± 2
		$H_{2,6}$, 7.37	bS	

[a] Symbols: M, multiplicity; S, singlet; D, doublet; T, triplet; Q, quartet; m, complex multiplet; b, broad. [b] In nitromethane.

marked differences, if any, in the reaction rates. Indeed, one should consider the possibility that replacement of iodide by the amines proceeds through ionization of the halogen in the rate-determining step. Although such a mechanism would seem rather unlikely in a medium of low polarity, it would explain the apparent uniformity in reaction rates. On the other hand, rate-determining nucleophilic displacement of iodide by amine can be reconciled with the synthetic results, if one considers the fact that alkyl substitution on pyridine produces only a relatively narrow range of basicities, perhaps not sufficiently large to produce differentiation in yields in the reaction times employed here. It is more noteworthy that even 2,6-lutidine reacts essentially completely to give a bis(lutidine)-boron cation, in spite of the likelihood that in this compound the substantial crowding around the boron atom should hinder the formation of the product. It appears, therefore, that steric inhibition in any of the reaction steps (eq 1–3), which is probable when the amine is 2,6-lutidine, is not large enough to interfere with a successful synthesis of the bis-amine cation.

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The Preparation of Germyl Methyl Sulfide and the Proton Nuclear Magnetic Resonance Spectra of Some Sulfur Derivatives of Silane and Germane[1]

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Germyl methyl sulfide has been prepared by the reaction of CH_3SNa with either GeH_3I or GeH_3Cl. Some of its physical and chemical properties have been determined. The compound is thermally stable at room temperature but decomposes in the presence of B_2H_6 or BF_3 to form GeH_4 and an unidentified solid material. The high-resolution proton nuclear magnetic resonance spectra of various sulfur derivatives of silane and germane have been obtained and are discussed.

Relatively few investigations on the synthesis and properties of sulfur derivatives of monogermane have ever been reported in the literature. The paucity of information on these systems is largely related to problems associated with their synthesis, low volatility, and questionable thermal stability. Until recently, the only known derivative of this type was digermyl sulfide, $(GeH_3)_2S$.[2,3] Although a detailed Raman–infrared

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[1] Presented, in part, at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967.

[2] S. Sujishi, Abstracts of the XVIIth International Congress of Pure and Applied Chemistry, Munich, 1959, p 53.

[3] T. D. Goldfarb and S. Sujishi, *J. Am. Chem. Soc.*, **86**, 1679 (1964).

study has been carried out on this compound,[3] very few of its physical or chemical properties are known. In two previous communications, we reported proton nuclear magnetic resonance (nmr)[4] and some Lewis base strength data[5] for the new compound germyl methyl sulfide, GeH_3SCH_3. In the present paper we report more details on the synthesis and some additional properties of this compound.

Previous nmr work from this laboratory on some of the simple oxygen derivatives of silane and germane pointed out some unusual proton chemical shift trends.[6,7] In order to see if analogous trends exist for the sulfur analogs, we have obtained high-resolution proton nmr data for most of the known sulfur derivatives of silane and germane.

Experimental Section

Apparatus.—All work was carried out in a Pyrex-glass vacuum system. Apparatus and techniques employed were identical with those previously described.[7,8]

Materials.—Commercial CH_3SH (purity confirmed by its infrared spectrum[9]), $(CH_3)_2S$ (mol wt: found, 61.6; calcd, 62.1), and BF_3 (mol wt: found, 67.9; calcd, 67.8; purity confirmed by its infrared spectrum[10]) were used after purification in the vacuum line. CH_3SNa was prepared from CH_3ONa and CH_3SH.[11] GeH_4 (mol wt: found, 76.6; calcd, 76.6; purity confirmed by its infrared spectrum[12]) was prepared from GeO_2 and $NaBH_4$.[13,14] GeH_3Cl and GeH_3I (purities confirmed by their infrared spectra[15]) were obtained by the reactions of GeH_4 with HCl[16] and I_2,[2,15] respectively. $(GeH_3)_2S$ (vapor pressure at 0°, 4.7 mm; lit.[2,3] 5.0 mm; purity confirmed by its infrared spectrum[3]) was prepared from GeH_3I and red HgS.[2,3] SiH_3SCH_3 (vapor pressure at 0°, 105.2 mm; lit.[17] 105.2 mm; purity confirmed by its infrared spectrum[17]) was prepared by the reaction of CH_3SH with the $(CH_3)_3N$ adduct of SiH_3I.[17] B_2H_6 (purity confirmed by its infrared spectrum[18]) was prepared by the reaction of $NaBH_4$ with H_2SO_4.[19]

Preparation of GeH_3SCH_3.—This compound was prepared by the reaction of CH_3SNa with either GeH_3Cl or GeH_3I. We recommend the use of GeH_3I, since it is much easier to purify than GeH_3Cl. GeH_3I (3.5 mmol) was condensed into a 250-ml round-bottom flask which contained approximately 1 g of freshly prepared CH_3SNa. The reaction flask was allowed to warm to room temperature, open to a trap maintained at −196°. All of the material which distilled out of the flask during the slow warming process was then condensed back and the procedure was repeated. This was done four times. No noncondensable material was formed in the reaction. The volatile products were then allowed to distil through traps at −46 and −64° and into a trap at −196°. Most of the material remained in the trap at −64° and was identified as impure GeH_3SCH_3 by its infrared spectrum and gas chromatogram.[20] A second preparation of GeH_3SCH_3 was carried out with GeH_3Cl (5.7 mmol) before final purification of the compound was attempted. The combined crude samples of GeH_3SCH_3 were purified by gas chromatography employing a 5 ft × $^1/_4$ in. glass column packed with benzyl ether (20%) on Chromosorb W support (60–80 mesh). When operating the chromatograph at a 100 cc of helium min^{-1} flow rate and a column temperature of 30°, the retention time of GeH_3SCH_3 was 6.5 min. The gas-phase molecular weight of the GeH_3SCH_3 recovered (4.23 mmol, average yield 46%) was 122.7 (calcd 122.7). Its melting point was −97° (±0.4°). *Anal.*[21] Calcd for CH_6GeS: C, 9.79; H, 4.93. Found: C, 9.72; H, 4.90.

Vapor Pressure of GeH_3SCH_3.—The vapor pressures of GeH_3SCH_3 at a number of temperatures were measured by a mercury manometer. The inner surface of the manometer had been pretreated with a separate sample of GeH_3SCH_3 for several hours. Data are recorded in Table I. Vapor pressures in the range −50.2 to +18.4° are given by the equation

$$\log P_{\mathrm{mm}} = -\frac{1537.9}{T} + 7.1555$$

which gives an extrapolated boiling point of 87°, a molar heat of vaporization of 7040 cal, and a Trouton constant of 19.6 cal deg^{-1} mol^{-1}.

TABLE I

VAPOR PRESSURES OF GeH_3SCH_3[a]

	P, mm			P, mm	
Temp, °C	Obsd	Calcd	Temp, °C	Obsd	Calcd
−50.2	2.0	1.8	+18.4	76.9	76.0
−36.6	4.4	4.5	+5.2[b]	43.0	42.7
−25.8	8.3	8.7	0.0[b]	34.2	33.5
−20.3	11.2	11.8	−8.6[b]	22.5	22.0
−17.8	13.3	13.6	−26.6[b]	8.6	8.3
−12.8	17.8	17.7	−36.8[b]	4.5	4.5
−4.2	27.2	27.4	−196[b]	0	
+11.0	56.6	55.4			

[a] Duration of the experiment was approximately 10 hr. The infrared spectrum of the sample at the end of the experiment was identical with that of the pure material. [b] Pressure observed on decreasing the temperature.

Thermal Stability of GeH_3SCH_3.—A sample of pure GeH_3SCH_3 (0.12 mmol; vapor pressure at 0°, 34.0 mm; calcd, 33.5 mm) was allowed to stand at room temperature partly in the liquid phase and partly in the vapor phase in a 9-cc all-glass break-seal exposed to normal laboratory lighting conditions for 7 days. The sample remained colorless throughout this time period, and no noncondensable material was formed. The infrared spectrum of the GeH_3SCH_3 recovered (0.11 mmol; vapor pressure at 0°, 35.0 mm) was identical with that of the pure sample. No residue was observed in the break-seal tube.

Infrared and Mass Spectra of GeH_3SCH_3.—The infrared absorption spectrum of GeH_3SCH_3 at pressures of 0.5 and 1.5 mm was determined on a Perkin-Elmer Model 137B Infracord spectrophotometer. A 10-cm gas sample cell fitted with KBr windows was employed for the measurements. The absorption maxima and some tentative assignments are given in Table II. The spectrum is shown in Figure 1.

The mass spectra of all germyl compounds are complex, mainly owing to the existence of five isotopes of germanium in significant natural abundance. A convenient way of providing information

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(19) W. L. Jolly, "Synthetic Inorganic Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1960, p 158; H. G. Weiss and I. Shapiro, *J. Am. Chem. Soc.*, **81**, 6167 (1959).

(20) Preliminary vpc separations were carried out by using a 20 ft × $^3/_8$ in. aluminum column packed with Carbowax 400 (25%) on Chromosorb W support (60–80 mesh) at 37°. A helium flow rate of 100 cc/min was maintained. Under these conditions, GeH_3SCH_3 had a retention time of 86 min. Small impurity peaks were observed at 4, 14, 24, and 47 min.

(21) Analysis performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

TABLE II

INFRARED ABSORPTION MAXIMA OF GeH_3SCH_3

Cm^{-1}	Tentative assignment	Analogy
3049 sh		
2979 w	C–H str[a]	
2891 sh		
2073 s	Ge–H str	2110 in $(GeH_3)_2S$[b]
1439 sh		
1433 w	CH_3 def	1440, 1320 in SiH_3SCH_3[c]
1322 1308 d, w		
1125 vw	Unassigned	
951 w	CH_3 rock	963 in $(CH_3S)_4Ge$[d]
883 m		
869 859 d, m	GeH_3 def	872, 849, 823, 816 in $(GeH_3)_2S$[b]
828 820 d, vs		
712 w	Unassigned	
694 w	C–S str	694 in $(CH_3)_2S$[e] 695 in SiH_3SCH_3[c]

[a] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954. [b] Reference 3. [c] Reference 17. [d] K. A. Hooton and A. L. Allred, *Inorg. Chem.*, **4**, 671 (1965). [e] I. F. Trotter and H. W. Thompson, *J. Chem. Soc.*, 481 (1946).

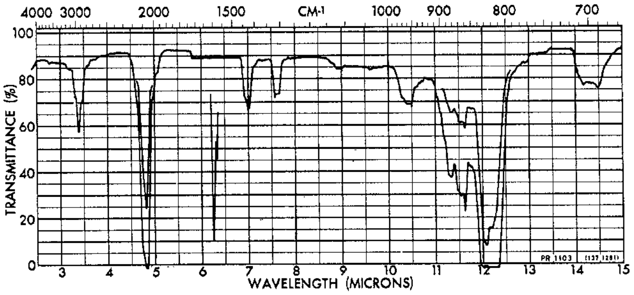

Figure 1.—Infrared absorption spectrum of GeH_3SCH_3. Peak at 1601 cm^{-1} is a polystyrene calibration.

about the major fragmentations of these compounds has been to group the peaks according to ions which have a common heavy-atom skeleton.[22] The heavy-atom skeleton is used as a label for the group. Thus, GeS^+ refers to all ions between *m/e* 102 ($^{70}Ge^{32}S$) and 111 ($H_3{}^{76}Ge^{32}S$). The mass spectrum of GeH_3SCH_3, obtained on a Consolidated Electrodynamics Corp. Model 103 C mass spectrometer operating at 70 V, consisted of four major groups of peaks with the relative intensities: $GeSC^+$ (100), GeS^+ (87), Ge^+ (69), and CS^+ (27). Several weak peaks were observed in the *m/e* 150–160 region (possibly due to $H_3GeSSCH_3$) and also in the *m/e* 82–94 region (CGe^+ rearrangement fragment).

Interaction of GeH_3SCH_3 and BF_3.—GeH_3SCH_3 (1.0 mmol) and BF_3 (1.0 mmol) were combined, mixed, and allowed to stand at −78° for 12 hr in a 5-cc all-glass break-seal tube. No noncondensable material was observed when the tube was opened; a white deposit which turned yellow after about 30 min remained in the vessel when all of the volatile products were removed. The latter could not be completely separated by low-temperature fractionation, but were identified as GeH_4 and unreacted BF_3 and GeH_3SCH_3 by infrared spectroscopy.[10,12] A yellow-orange solid material continued to form in the traps as the fractionations were attempted. No absorptions which could be ascribed to GeH_3F were observed in the infrared spectrum of the products.[15]

Interaction of GeH_3SCH_3 and $(GeH_3)_2S$ with B_2H_6.—The interactions of GeH_3SCH_3 and $(GeH_3)_2S$ with B_2H_6 were carried out in a small tube attached to a mercury manometer. In each case, the pressures of the individual components of the mixtures were measured in the reaction tube prior to any combination. The temperature of the mixtures was raised to −79° then lowered to −196° several times in order to facilitate mixing. At −79.0°, B_2H_6 was present in the gas phase; all sulfides were in the liquid phase.

When GeH_3SCH_3 (0.63 mmol) and B_2H_6 (0.34 mmol) were allowed to interact at −79.0°, the pressure of the system did not come to an equilibrium value but continued to increase slowly. After 7 hr the pressure was 123.9 mm and still increasing. The sum of the individual vapor pressures at this temperature was 99.3 mm. The volatile material (0.029 g) which distilled out of the reaction tube maintained at 130° could not be separated further in the vacuum line but was identified as a mixture of B_2H_6 and GeH_4 from an infrared analysis.[12,18] On raising the temperature of the reaction tube to between −79 and 0° for 11 hr, an additional amount of GeH_4 (0.0148 g) was recovered. When the GeH_4 formation ceased, a yellow-white solid material remained in the reaction tube which, on pumping at room temperature, yielded a very small amount of unidentified volatile material, the infrared spectrum of which was very similar to the original GeH_3SCH_3. The solid material acquired an orange color on exposure to air and its infrared spectrum (KBr pellet) indicated both C–H and Ge–H bonds present. However, owing to the apparent instability of the material, it was not further characterized.

On combining $(GeH_3)_2S$ (0.72 mmol) and B_2H_6 (0.35 mmol) in a similar reaction system, a constant pressure of 96.8 mm at −79.0° was observed after 3 hr. An equivalent amount of pure B_2H_6 exerted a pressure of 98.0 mm at this temperature. The vapor pressure of $(GeH_3)_2S$ at this temperature is negligible. On lowering the temperature to −130.8°, the pressure of the mixture dropped to 44.5 mm after about 15 min. An equivalent amount of B_2H_6 exerted a pressure of 44.3 mm under these conditions. The mixture acquired a yellow color in the above studies. The material (0.011 g) which distilled out of the reaction tube maintained at −130.8° was mainly B_2H_6 with a small amount of GeH_4 (both identified by their infrared spectra[12,18]). The material which remained in the vessel was unreacted $(GeH_3)_2S$ (~0.7 mmol; vapor pressure at 0°, 5.3 mm; lit. 5.0 mm; confirmed by its infrared spectrum[3]) and a very small amount of yellow solid material.

Proton Nmr Studies of $(CH_3)_2S$, SiH_3SCH_3, GeH_3SCH_3, and $(GeH_3)_2S$.—High-resolution proton nmr spectra of the listed compounds were obtained on a Varian Associates A-60 spectrometer operating at room temperature. Samples were sealed *in vacuo* in standard thick-walled tubes. Cyclohexane was used as solvent, with a drop of tetramethylsilane added as an internal standard; 90 and 20% concentrations (by volume) were studied; chemical shifts listed in Table III are extrapolated to infinite dilution. On changing the concentration from 90 to 20%, τ of the CH_3 groups increased by approximately 0.03 ppm, τ of the SiH_3 group by 0.02 ppm, and τ of the GeH_3 groups by approximately 0.09 ppm.

Results and Discussion

Synthesis and Properties of GeH_3SCH_3.—Germyl methyl sulfide has been prepared in good yield by the reaction of solid CH_3SNa with either GeH_3I or GeH_3Cl

$$\mathrm{CH_3SNa + GeH_3I \longrightarrow GeH_3SCH_3 + NaI} \qquad (1)$$

Under the experimental conditions employed in this work, the pure compound was thermally stable and could be purified by gas chromatography. It is much more stable than the corresponding oxygen derivative GeH_3OCH_3, which was found to decompose even at temperatures below −23°.[8] It seems to be a general rule that germyl compounds derived from the second-

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(22) S. Cradock, E. A. V. Ebsworth, G. Davidson, and L. A. Woodward, *J. Chem. Soc., A*, 1229 (1967).

row elements are more thermally stable than those derived from first-row elements. Thus $(GeH_3)_3P$ is known and has been characterized,[22] whereas $(GeH_3)_3N$ has not been successfully prepared.[23] Although both $(GeH_3)_2O$ and $(GeH_3)_2S$ are known, the latter appears to be much more stable than the former.[3] Little information is available on the relative thermal stabilities of GeH_3F and GeH_3Cl.

In the presence of B_2H_6, both GeH_3SCH_3 and $(GeH_3)_2S$ decompose to form GeH_4 and an unidentified solid material. The decomposition takes place at low temperatures and is more rapid with GeH_3SCH_3 than it is with $(GeH_3)_2S$. Germyl methyl sulfide also decomposes in a similar manner in the presence of BF_3.

Very little can be concluded about the decomposition of $(GeH_3)_2S$ from the results of the present work; however, Sujishi and Zafonte[24] have carried out a more detailed analysis of this decomposition. Their observations of GeH_4 formation from $(GeH_3)_2S$ in the presence of B_2H_6 are in agreement with ours, but a more detailed analysis of the products suggests that the formula of the solid material in the reaction is GeH_2S. The decomposition is given by

$$(GeH_3)_2S \longrightarrow GeH_4 + GeH_2S(s) \tag{2}$$

In the analogous GeH_3SCH_3 decomposition, since the solid material contained both C–H and Ge–H bonds, a reasonable reaction scheme which would qualitatively account for the results consists of intermolecular condensations of the type shown in eq 3. However, a

$$2GeH_3SCH_3 \longrightarrow GeH_4 + GeH_2(SCH_3)_2 \tag{3}$$

complete analysis of the condensation products has not been carried out.

The purpose of studying the interaction of B_2H_6 with $(GeH_3)_2S$ and GeH_3SCH_3 was an attempt to investigate the Lewis basicity of the sulfur atom in the Ge–S–Ge and Ge–S–C linkages. No base properties were detected under the conditions used and owing to the irreversible decomposition of the compounds in the presence of B_2H_6, no further work was carried out. In the hydrogen-bonding studies previously reported for these compounds, no decomposition reactions were observed. The results indicated that both $(GeH_3)_2S$ and GeH_3SCH_3 are weaker bases than $(CH_3)_2S$, in accord with the present results. The relative basicities of the two germanium compounds could not be distinguished.

TABLE III

PROTON NMR DATA FOR DIMETHYL SULFIDE AND SOME SULFUR DERIVATIVES OF SILANE AND GERMANE

	τ $(\pm 0.01)^a$		$J_{H-H'}$ (± 0.05),	$J_{^{13}CH}$ (± 0.5),
Compound	CH_3	SiH_3 or GeH_3	cps	cps
$(CH_3)_2S$	7.98	...	0.30^b	137.8
$SiH_3SCH_3{}^d$	7.98	5.71	0.45	141.0
$(SiH_3)_2S^c$	...	5.65	0.70	...
GeH_3SCH_3	7.95	5.52	0.60	140.3
$(GeH_3)_2S$	...	5.38	...	...

[a] Values extrapolated to infinite dilution. [b] N. Van Meurs, *Spectrochim. Acta*, **19**, 1695 (1963). [c] E. A. V. Ebsworth and J. J. Turner, *J. Chem. Phys.*, **36**, 2628 (1962), $J_{^{29}SiH} = 224.0$ $\pm 0.3)$ cps. [d] $J_{^{29}SiH} = 218.5\ (\pm 0.4)$ cps.

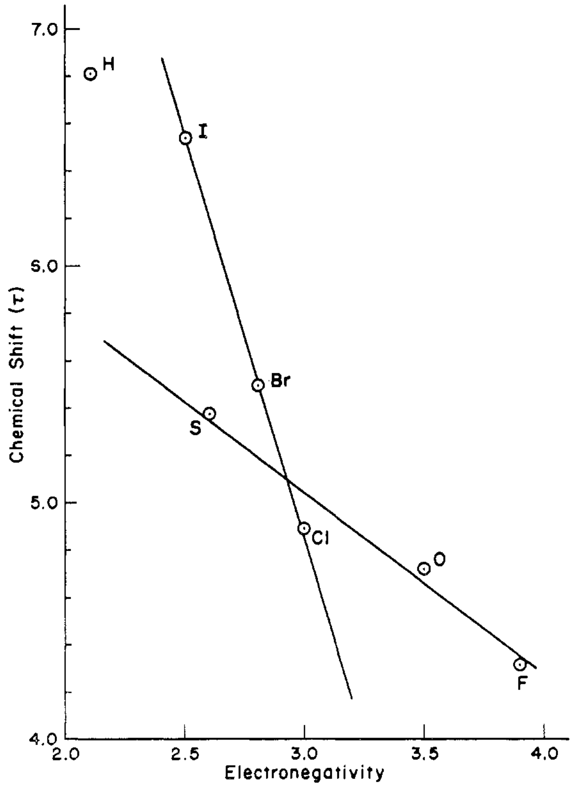

Figure 2.—Variation of the proton chemical shift of GeH_3 compounds with the electronegativity of the substituent. For electronegativities we have used the "best values" of Pritchard and Skinner.[28]

Proton Nmr Studies of Some Sulfur Derivatives of Silane and Germane.—Proton nmr data for $(CH_3)_2S$ and most of the known sulfur derivatives of SiH_4 and GeH_4 are given in Table III. The variation of the chemical shifts of the methyl protons in the CH_3SMH_3 (M = C, Si, and Ge) series of compounds is somewhat different from the variation of the methyl chemical shifts in the corresponding oxygen derivatives. In the oxygen series, the methyl resonance of $(CH_3)_2O$ is at the highest field (τ 6.79)[25] while that of CH_3OGeH_3 is at the lowest field (τ 6.51)[6] and that of CH_3OSiH_3 (τ 6.58)[26] is intermediate, but closer to CH_3OGeH_3. In the sulfur series the methyl resonance of GeH_3SCH_3 falls to the low field of $(CH_3)_2S$ by 0.03 ppm, but SiH_3SCH_3 and $(CH_3)_2S$ have identical chemical shifts. Since both GeH_3SCH_3 and SiH_3SCH_3 act as weaker Lewis bases than $(CH_3)_2S$,[5] the position of the methyl resonance is clearly not sensitive to changes in basicity of the sulfur atom in the molecules. The insensitivity of the CH_3S proton resonance to the nature of the group to which sulfur is attached has also been observed in the nmr study of $(CH_3)_3SiSCH_3$ and $(CH_3)_3GeSCH_3$.[27]

Electronegativity considerations are normally of concern in the interpretation of chemical shift data.

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(24) S. Sujishi and L. Zafonte, private communication.

(25) S. G. Frankiss, *J. Phys. Chem.*, **67**, 752 (1963).

(26) C. H. Van Dyke and A. G. MacDiarmid, *Inorg. Chem.*, **3**, 1071 (1964).

(27) K. A. Hooton and A. L. Allred, *ibid.*, **4**, 671 (1965).

Since oxygen is more electronegative than sulfur,[28] it is not surprising to find that the C–H, Si–H, and Ge–H proton resonances in the ether derivatives are found at lower fields than they are for the corresponding thio derivatives.[29] The difference in chemical shifts between the oxygen and sulfur systems is greatest for the C–H protons followed by Ge–H protons and the least amount of change is observed for the Si–H protons. This trend is also observed in comparing electronegativity and proton nmr data for the halide derivatives of CH_4, SiH_4, and GeH_4.[30]

Ebsworth and Turner[31] have pointed out that for a series of SiH_3 compounds, there is a general decrease of τ_{SiH} as the electronegativity of the substituent increases. A similar relationship is found for CH_3 compounds.[32] However, plots of electronegativity *vs.* chemical shift values for the two series of compounds differ quite significantly.[31] One of the key differences in the two systems occurs with the sulfur derivatives. The chemical shift of $(CH_3)_2S$ is very close to that of CH_3I (sulfur and iodine have about the same electronegativity values, 2.5–2.6); however, the chemical shifts of $(SiH_3)_2S$ (τ 5.65) and SiH_3I (τ 6.56) are significantly different. In the present work, we wanted to ascertain the position of $(GeH_3)_2S$ with respect to GeH_3I. A plot of the proton chemical shifts of most of the known GeH_3 compounds *vs.* electronegativity of the substituents is given in Figure 2.[33] The pattern obtained is strikingly similar to that of the analogous plot for SiH_3 compounds.[31] Thus, we conclude that when considering electronegativity effects alone, the chemical shifts of SiH_3 and GeH_3 compounds follow similar trends, which are different in certain respects from trends of simple carbon compounds. We prefer to delay an explanation of the differences until the factors which determine the Si–H and Ge–H chemical shifts are better understood.

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Nuclear Magnetic Resonance Chemical Shifts of the Acid Protons in Silyl-Substituted Benzoic Acids and Phenols and the Question of ($\pi \rightarrow$ d)–π Interaction in the Silicon–Phenyl Bond[1]

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The electrical effects of *para*- and *meta*-substituted trimethylsilylphenols and -benzoic acids have been investigated by nmr techniques designed to elucidate these effects in the ground-state, neutral molecules, and the data have been compared to those for phenol and benzoic acid themselves and for the *p*- and *m*-*t*-butyl derivatives. Results from measurement of the chemical shifts of the acidic protons of the substituted benzoic acids in an inert solvent (CCl_4) give the same order of hydrogen bonding as for the strong donor solvent pyridine: H > *m*- and *p*-*t*-butyl > *p*- and *m*-trimethylsilyl. For the analogous phenols the hydrogen-bonding strength in both types of solvents decreases, H > *p*-trimethylsilyl, but while *p*-trimethylsilylphenol is weaker than *p*-*t*-butylphenol in dilute solution in carbon tetrachloride, the reverse order is observed in dimethyl sulfoxide.

We have been led to take an agnostic view toward supposed large (p $\rightarrow$ d)–π contributions to the bonds silicon forms with nitrogen on the basis of experiments involving nuclear magnetic resonance techniques.[3] Apart from the silicon–nitrogen bond, convincing evidence for large π interactions in fourth-group bonds comes from studies of silicon–phenyl systems. Here the argument involves the electrical effect of silicon as a substituent. Current electronegativity tables agree that the silicon atom should donate electrons to the phenyl group. Should there be large ($\pi \rightarrow$ d)–π interactions in the silicon–phenyl bond, however, then this inductive electron release would be offset by the drift of π-electron density from the phenyl ring, and the result might be a net reversal of the expected electrical effect of the silicon atom.

In their classic paper Chatt and Williams reported the results of a careful study of the strengths of the acids

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