

anisms may also contribute to the STHF, this value should be regarded as giving only a rough upper limit for such a direct metal-metal interaction.

Conclusions

This work has demonstrated the feasibility of determining magnetic parameters in dimeric copper(II) alkanoates from epr studies of polycrystalline samples. It appears likely that the techniques discussed here can be generalized to other dimeric or even polymeric cluster complexes. For these systems, the magnetic parameters may be derived by several different methods depending upon the relative magnitudes of the anisotropic spin-spin coupling parameter, D , and the microwave energies employed. If the two energies are comparable, a measurement of the high-field spectrum at two different microwave frequencies should suffice. If the spectrometer frequency corresponds to an energy sufficiently greater than D , unambiguous high- and low-field spectra as well as a zero-field spectrum obtain. For such a case, a study at a single microwave frequency would serve to determine, and possibly overdetermine, the magnetic parameters. Studies at higher microwave frequencies have the additional advantage in providing more accurate data owing to the smaller fractional line widths.

Our studies of copper propionate monohydrate are in accord with previous single-crystal epr investigations of copper(II) alkanoate systems in that the g values for the copper-copper pairs agree with those of the copper-zinc pairs. For these systems, only a single-frequency X-band study of the $S = 1/2$ and the high-field $S = 1$

spectra is required for the specification of all of the magnetic parameters. Furthermore, a comparison of the hyperfine splitting for the $S = 1$ and $S = 1/2$ species may provide information regarding the supertransferred hyperfine field. Extension of this doping technique to other cluster complexes must await appropriate single-crystal studies on model complexes.

The weakly coupled model has been found to give a satisfactory account of the experimental data for $\text{Cu}(\text{Pro})_2$ as well as for other copper(II) alkanoates. In this connection, it is of interest to consider the relationship between the metal-metal distance and the nature of the bonding. In the model complex copper acetate monohydrate, the internuclear distance is 2.64 Å. A recent calculation by Schleuter, Jacobsen, and Rundle⁴³ has shown that, at this distance, the overlap between corresponding copper(II) 3d orbitals is quite small. Although the internuclear distance in the copper(II) alkanoates is only about 0.1 Å larger than that found in copper metal, a somewhat more meaningful comparison may be made by considering the bond length in the Cu_2 molecule. For this molecule, Hare, Sleight, Cooper, and Clarke⁴⁴ have estimated that the highest filled σ molecular orbital contains only about 7% $3d_{z^2}$ character and that this value occurs at an internuclear separation of 2.19 Å. Thus, the much larger distance found in the copper(II) alkanoates would seem to rule out the existence of a strong direct metal-metal interaction.

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The Preparation and Properties of Methyl(germyl)silanes and Some Related Compounds¹

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Methyl(germyl)silanes, $(\text{CH}_3)_n\text{Si}(\text{GeH}_3)_{4-n}$ in which $n = 0, 1, 2,$ or 3 , have been synthesized by the reaction of sodium germly with the appropriate methylchlorosilane. The related compounds 1,1,1-trimethyldigermane, digermane, and germlysilane have been prepared by the reaction of sodium germly with trimethylfluorogermane, bromogermane, and bromosilane, respectively. The new compounds, except tetragermlysilane, have been characterized by elemental analysis and measurement of their molecular weights, vapor pressures, and melting and boiling points. Proton nmr spectra of the neat liquids have been recorded and the results are interpreted in terms of inductive and anisotropic effects. Infrared spectra in the range $4000\text{--}650\text{ cm}^{-1}$ have been measured on samples in the gas phase and frequency assignments have been made.

Introduction

The use of alkali metal derivatives of germane, M^+GeH_3^- , in which M is the alkali metal, for the

(1) Based in part on a thesis submitted by W. A. Dutton to the Faculty of Graduate Studies and Research of McGill University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. This work was presented in part at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964.

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preparation of compounds containing the GeH_3 group has not yet been fully explored. Alkylgermanes, $\text{C}_n\text{H}_{2n+1}\text{GeH}_3$, in which $n = 1, 2,$ or 3 , have been synthesized by the reaction of sodium germly with alkyl halides in liquid ammonia as solvent.³

More recently, Van Dyke and coworkers have demonstrated the advantages of hexamethylphosphor-

(3) G. K. Teal and C. H. Kraus, *J. Am. Chem. Soc.*, **72**, 4706 (1950).

amide as a solvent for the preparation of sodium and potassium germyl and for their reactions with alkyl halides.⁴ Also, Jolly, *et al.*,⁵ have shown that germane, like other weak acids, is deprotonated with a slurry of powdered potassium hydroxide in 1,2-dimethoxyethane and the resulting GeH_3^- is alkylated with methyl iodide to give an 80% yield of methylgermane.

The possibility that solvent-free sodium germyl might couple with germyl and silyl halides which react with ammonia, hexamethylphosphoramide, or potassium hydroxide has been investigated in this work. The reaction of sodium germyl with germyl bromide was tried first, but the yield of digermene was disappointingly low. Subsequently, sodium germyl was allowed to react with a series of methylchlorosilanes, $(\text{CH}_3)_n\text{SiCl}_{4-n}$, in which $n = 1, 2, \text{ or } 3$, and silicon tetrachloride; the corresponding methyl(germyl) silanes were produced in good yield, but only minute amounts of tetragermylsilane were obtained. These successful preparations prompted us to attempt the reaction of sodium germyl with silyl bromide and trimethylgermyl fluoride. Germylsilane, first prepared by an electric-discharge method,⁶ and 1,1,1-trimethyldigermene resulted.

Experimental Section

Apparatus.—All preparations were done with a high-vacuum manifold, the stopcocks and ground-glass joints of which were lubricated with Kel-F Fluorocarbon grease, and standard vacuum system techniques were used. Volatile materials were purified by low-temperature fractionation in a column similar to that described by LeRoy⁷ or in traps surrounded by suitable slush baths. When repeated distillations were unsuccessful, purifications were done by vapor phase chromatography (vpc) using an infrared spectrophotometer set at 2050 cm^{-1} (the Ge-H stretching frequency) as the detector of compounds containing Ge-H bonds. Thermal conductivity detectors normally used in vpc were unsuitable because methyl(germyl)silanes decompose on them. The column, 17 mm in internal diameter and 8 ft long, was packed with 20% by weight of silicone grease on acid-washed firebrick (Matheson Coleman and Bell; 40-60 mesh). This column was used at room temperature with a nitrogen flow rate of about 700 ml/min.

Infrared spectra were recorded on a Perkin-Elmer Model 137 or Model 421 spectrophotometer, using 10-cm gas cells fitted with NaCl or KBr windows. Spectra were recorded only on samples in the gas phase in order to facilitate recovery of the small amount of sample usually available.

Proton nuclear magnetic resonance (nmr) spectra were taken on a Varian Associates HR-60 spectrometer operated at 60 Mc. A dilute solution of tetramethylsilane (TMS) in carbon tetrachloride was used as an external standard (τ 10.00 ppm), and calibration was done by means of 60-cps side bands on the TMS peak. Duplicate measurements were made on a Varian A-60 spectrometer equipped with an automatic integrator. Samples of the neat liquids were sealed in fine capillary tubes which were then placed in standard nmr tubes containing dilute TMS.

A drybox filled with purified nitrogen was used to handle alkali metals.

Materials.—Germane was prepared in 90-95% yield by refluxing germanium dioxide in 1 *M* hydrobromic acid for 6 hr and

then adding an excess of aqueous sodium borohydride.^{8,9} The crude product was trapped at -196° and purified by distillation at -150° .

Bromogermene, GeH_3Br , was obtained by the direct interaction of equimolar amounts of bromine and germane.⁹ This reaction produces a mixture of bromogermenes from which monobromogermene can be easily separated by low-temperature fractionation. The yield of pure monobromogermene was usually greater than 50%.

Sodium germyl was prepared according to the method of Kraus and Carney¹⁰ by bubbling a measured excess of germane through a solution of sodium in liquid ammonia at -45° . The liquid ammonia was pumped off at -45° , and then the ammonia of crystallization was removed by prolonged pumping at -23° . The resulting white, ammonia-free sodium germyl was stored at -78° under vacuum until it was used in a reaction.

Commercial samples of the methylchlorosilanes (Dow Corning, Purified grade) and silicon tetrachloride (Fisher, Reagent grade) were fractionally distilled immediately before use. Trimethylfluorosilane was prepared by the interaction of hexamethyldisiloxane with boron trifluoride.¹¹ Bromosilane was obtained by the cleavage of phenylsilane with hydrogen bromide.¹² Trimethylbromogermene was synthesized by the reaction of tetramethylgermane with hydrogen bromide.¹³ The reaction of hexamethyldigermoxane with germanium tetrafluoride was used to prepare trimethylfluorogermene.¹⁴

The purities of all volatile compounds were checked by molecular weight, vapor pressure, and infrared spectral measurements.

Results

Preparations. Digermene.—The best yield of crude digermene (0.28 mmol; 6.8% yield) was obtained when an excess of bromogermene (5.68 mmol) was condensed on freshly prepared, ammonia-free sodium germyl (4.1 mmol), and the mixture was allowed to react at -45° and then at -23° for a total of 2 hr. The volatile products were separated by fractional distillation into two components: (i) the fraction volatile at -130° was germane (0.38 mmol; mol wt: found, 76.5; calcd, 76.6) and it accounted for 9.4% of the sodium germyl available; (ii) the fraction (0.28 mmol) volatile between -120 and -100° had the vapor pressure of digermene (found, 25.4 mm at -46° ; lit.,¹⁵ 24.0 mm at -46°) but its molecular weight was low (found, 137; calcd, 151.2), indicating the presence of an impurity. An infrared spectrum of this fraction contained two unidentified peaks (at 1141 and 828 cm^{-1}) in addition to those characteristic of pure digermene.¹⁶ All attempts to remove the unidentified impurity by fractional distillation were unsuccessful.

In another experiment a fivefold excess of bromogermene (23.3 mmol) over sodium germyl (4.2 mmol) was used to ensure a solid-liquid interaction. After this mixture was kept for 2 hr at -30° , the volatile product consisted of germane (1.42 mmol), a trace of digermene as indicated by infrared measurements, and unreacted bromogermene (19.7 mmol).

In further attempts to increase the yield of digermene,

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tetrahydrofuran, benzene, and diethylene glycol dimethyl ether were each used as a liquid medium for the reaction of bromogermane with sodium germyl, but in no case were measurable amounts of digermane produced.

Trimethyl(germyl)silane, $(\text{CH}_3)_3\text{SiGeH}_3$.—Trimethylchlorosilane (9.10 mmol) was condensed on ammonia-free sodium germyl (10.4 mmol) and the mixture was warmed during 4 hr from -23 to 0° . The volatile products were distilled through traps at -45 and -140° , and the fraction which condensed at -140° was distilled slowly at -78° until a fraction containing almost pure trimethyl(germyl)silane was obtained (1.10 mmol, 12% yield; mol wt: found, 148.0; calcd, 148.8). Since an infrared spectrum of this fraction showed an Si–O–Si stretching absorption band at 1080 cm^{-1} , the fraction was purified by vpc using the infrared detector, and a pure sample of trimethyl(germyl)silane was obtained. *Anal.*¹⁷ Calcd for $\text{C}_3\text{H}_{12}\text{GeSi}$: C, 24.21; H, 8.12; Si, 18.87. Found: C, 24.49; H, 8.08; Si, 18.76.

Trimethyl(germyl)silane was also prepared by the reaction of trimethylfluorosilane (6.37 mmol) with sodium germyl (5.50 mmol), using the procedure described above. The yield of crude product was 45% (2.4 mmol; mol wt: found, 148.5; calcd, 148.8).

Dimethyl(digermyl)silane, $(\text{CH}_3)_2\text{Si}(\text{GeH}_3)_2$.—An excess of dimethyldichlorosilane (5.50 mmol) was condensed on ammonia-free sodium germyl (7.2 mmol), and the mixture was warmed from -23 to $+2^\circ$ over 3 hr. The product mixture was separated by distilling it through traps at -23 , -45 , and -130° . Unreacted dimethyldichlorosilane (2.66 mmol) was held at -130° , and dimethyl(digermyl)silane (1.00 mmol, 28% yield; mol wt: found, 208.8; calcd, 206.4) was retained in the -23° trap. The final purification was done by flashing off vapor at 0.7° until the vapor pressure at this temperature became constant at 6.28 ± 0.05 mm. *Anal.* Calcd for $\text{C}_2\text{H}_{12}\text{Ge}_2\text{Si}$: C, 11.48; H, 5.78; Si, 13.42. Found: C, 11.45; H, 5.54; Si, 13.73.

Methyl(trigermyl)silane, $\text{CH}_3\text{Si}(\text{GeH}_3)_3$.—A yield of 34.4% was obtained when methyltrichlorosilane (9.10 mmol) was condensed on sodium germyl (12.0 mmol), and the mixture was warmed slowly from -23 to $+9^\circ$ over 4.5 hr. Methyl(trigermyl)silane (1.37 mmol) was retained in a trap at -23° . The final purification was done by flashing off vapor at 0.6° until the vapor pressure at this temperature was 1.60 ± 0.05 mm. This compound is not sufficiently volatile at 25° for accurate gas-phase measurement of its molecular weight. *Anal.* Calcd for $\text{CH}_{12}\text{Ge}_3\text{Si}$: C, 4.45; H, 4.48; Si, 10.40; Ge, 80.66. Found: C, 4.38; H, 4.70; Si, 10.64; Ge, 80.51.

Tetragermysilane, $\text{Si}(\text{GeH}_3)_4$.—A large excess of silicon tetrachloride (10.1 mmol) was condensed on ammonia-free sodium germyl (13.7 mmol) and the mixture was warmed from -23 to -1° over a 4-hr

period. The products were distilled until a small involatile drop of liquid was left in a trap at -23° . This liquid had a vapor pressure of less than 2 mm at 25° . Its melting point was $-53.3 \pm 0.4^\circ$, the average of three measurements. After nine similar preparations, the total amount of material prepared was only 18 mg. An infrared spectrum of its gaseous phase showed only two main peaks characteristic of a molecule of tetrahedral symmetry: a strong band at 2072 cm^{-1} due to Ge–H stretching vibrations of the GeH_3 group and a very strong band at 772 cm^{-1} due to the symmetric GeH_3 deformation vibration. The identity of the compound was further confirmed by a measurement of its proton nmr spectrum. This consisted of one strong peak at τ 6.36 ppm due to the GeH_3 group and two weak peaks at τ 6.48 and 6.61 ppm attributed to an unidentified impurity.

A 15-mg sample was sent for microanalysis but this was not sufficient for a duplicate determination. The single determination done indicated no germanium and 10.9% H (calcd for $(\text{GeH}_3)_4\text{Si}$: Ge, 87.8; H, 3.66). These results must be erroneous as both infrared and proton nmr results prove without doubt the presence of the GeH_3 as the only functional group in this product which is, therefore, believed to be tetragermysilane.

Germysilane, GeH_3SiH_3 .—Bromosilane (7.7 mmol) was condensed on ammonia-free sodium germyl (11.9 mmol) and the reaction vessel was held at -78° for 16 hr and then at -45° for 1 hr; it was finally warmed from -23 to $+1^\circ$ over a 3-hr period. The crude product (0.6 mmole, 7.8% yield) was mainly germysilane as evident from its infrared spectrum which was identical with that reported by Spanier and MacDiarmid.⁶

1,1,1-Trimethyldigermane, $(\text{CH}_3)_3\text{GeGeH}_3$.—A yield of 36.4% was obtained when trimethylfluorogermane (2.6 mmol) was condensed on a large excess of sodium germyl (21.3 mmol). The temperature of the reaction vessel was raised from -20 to -4° over a period of 2 hr and maintained at about 0° for an additional 6 hr. The resulting trimethyldigermane (0.96 mmol; mol wt: found, 192.3; calcd, 193.3) was purified by vacuum distillation at -78° .

The same compound was also prepared in much lower yield (8.4%) when trimethylbromogermane (6.29 mmol) was condensed on ammonia-free sodium germyl (5.71 mmol) and allowed to react for 1 hr at -23° and then for 1 hr at 0° . Trimethyldigermane (0.48 mmol) was recovered and purified by vacuum distillation. *Anal.* Calcd for $\text{CH}_{12}\text{Ge}_2$: H, 6.25; C, 18.64; Ge, 75.10. Found: H, 6.50; C, 18.85; Ge, 75.07

Thermal Decomposition of Dimethyl(digermyl)silane.—After 18.5 hr at 85° , a sample (0.5 mmol) of dimethyl(digermyl)silane sealed in a 50-ml Pyrex tube was recovered unchanged. However, after 15 min at 200° , a metallic-like mirror covered the interior of the reaction vessel. The sample was kept in the oven at 200° for 19.5 hr to ensure complete decomposition.

(17) Elemental analyses were done by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

TABLE I
 PHYSICAL CONSTANTS OF THE NEW GERMYL COMPOUNDS

Compound	Mp, ^a °C	Bp, ^b °C	ΔH_v , ^c kcal mol ⁻¹	Trouton constant	Vapor pressure equation constants ^d		
					A	B	Temp range, °C
(CH ₃) ₃ SiGeH ₃	-77.4	73.6	7.24 ± 0.03	20.9	-1581.3	7.4413	15-41.5
(CH ₃) ₂ Si(GeH ₃) ₂	-93.1	116.3	8.22 ± 0.02	21.1	-1797.3	7.4955	24-116
CH ₃ Si(GeH ₃) ₃	-101.0	154.6	9.35 ± 0.02	21.9	-2044.1	7.6598	28-105
Si(GeH ₃) ₄	-53.3
(CH ₃) ₃ GeGeH ₃	-89.6	74.4	8.65 ± 0.05	24.9	-1889.3	8.3172	0-54

^a By the dropping plunger technique. ^b Calculated from the vapor pressure equation. ^c Calculated from the slope of a log p_{mm} vs. T^{-1} plot using the method of least squares. ^d In the equation $\log p_{mm} = [A/(t + 273.16)] + B$.

 TABLE II
 VAPOR PRESSURES OF THE NEW GERMYL COMPOUNDS

(CH ₃) ₃ SiGeH ₃			(CH ₃) ₂ Si(GeH ₃) ₂			CH ₃ Si(GeH ₃) ₃			(CH ₃) ₃ GeGeH ₃		
Temp, °C	P, mm		Temp, °C	P, mm		Temp, °C	P, mm		Temp, °C	P, mm	
	Obsd	Calcd		Obsd	Calcd		Obsd	Calcd		Obsd	Calcd
15.0	90.0	89.9	23.8	26.9	27.8	27.9	7.5	7.4	0.0	24.6	25.2
16.9	97.8	97.6	28.4	33.7	34.3	32.3	9.4	9.3	19.9	76.4	74.2
19.0	106.7	106.9	31.0	37.8	38.6	36.9	11.7	11.7	20.7	80.1	77.3
20.5	113.6	113.9	37.4	50.4	51.1	39.4	13.1	13.2	21.8	83.1	81.7
22.5	123.3	123.8	41.9	61.5	61.8	42.0	15.0	14.9	23.8	90.5	90.2
24.5	134.8	134.5	46.3	73.9	74.1	44.4	16.7	16.7	25.8	99.3	99.5
26.3	146.1	144.8	50.2	86.8	86.6	46.7	18.3	18.6	27.2	108.9	106.5
27.2	149.6	150.2	54.4	101.6	102.0	51.7	23.5	23.3	28.8	115.1	114.9
29.0	162.0	161.4	60.3	128.9	127.6	54.2	25.6	26.0	31.4	129.1	130.0
32.2	183.3	183.1	64.5	153.0	148.9	56.2	28.0	28.4	34.9	156.6	152.9
33.0	190.8	188.9	68.2	173.0	170.0	58.3	30.8	31.1	37.3	171.7	170.5
35.1	204.2	204.9	72.3	200.0	196.3	60.3	33.5	33.9	39.9	189.6	191.6
35.7	211.5	209.6	76.2	227.6	224.4	62.3	36.4	36.9	43.2	220.5	221.4
37.5	224.0	224.5	80.5	263.6	259.2	67.2	45.4	45.1	46.1	250.8	250.9
39.5	242.9	241.9	85.3	306.9	303.1	69.5	49.8	49.5	49.5	285.4	289.6
41.4	259.0	259.6	87.5	328.5	325.3	71.9	54.9	54.4	52.1	313.2	322.6
			93.9	401.2	397.3	74.8	61.3	61.0	54.0	340.1	348.7
			96.6	432.5	431.4	78.2	69.5	69.5			
			99.0	462.5	463.7	80.7	77.0	76.4			
			101.7	499.5	502.3	83.6	85.8	85.2			
			107.8	590.0	599.5	86.6	95.9	95.1			
						90.2	108.7	108.2			
						93.1	121.5	119.9			
						96.2	133.7	133.6			
						99.1	147.4	147.5			
						102.3	163.6	164.3			
						105.1	177.9	180.3			

The products, separated by fractional distillation, were hydrogen (0.25 mmol), germane (0.25 mmol; mol wt: found, 76.7; calcd, 76.6), and dimethylsilane, (CH₃)₂SiH₂ (0.49 mmol; mol wt: found, 62.9; calcd, 60.2).

Physical Properties.—The physical data obtained for all new compounds are listed in Tables I and II, the infrared absorption peaks and their assignments made by comparison with those of the methylsilanes^{18,19} are given in Table III, and the proton nmr chemical shifts are shown in Table IV.

Discussion

Reactions of Sodium Germlyl.—Although reactions of sodium germlyl are usually done with liquid ammonia as a solvent,³ it was not possible to use this solvent in the preparation of methylgermylsilanes because of its rapid reaction with the methylchlorosilanes. Attempts to use "inert" organic solvents such as benzene, tetrahydrofuran, and diglyme (diethylene glycol

dimethyl ether) were made in the preparation of digermene, and in no case was there any indication of an improved yield. Moreover, the addition of a large volume of a volatile solvent introduced the serious difficulty of separating and purifying the small amount of product formed. Because of these complications, it was decided to use solid, ammonia-free sodium germlyl in the absence of any solvent or liquid medium for all of the reactions. Low and often erratic yields were obtained, presumably because of poor contact between the reagents. The thermal instability of sodium germlyl¹⁰ was an additional complication which may have contributed to the generally low yields obtained. In spite of these limitations, the direct replacement of a halogen by a germlyl group occurs, usually in low yield. There was no evidence of partially substituted products in the preparation of the di-, tri- and tetragermlylsilanes, even though the halide starting material was usually present in excess.

Decomposition of Dimethyldigermylsilane.—At 200°, dimethyldigermylsilane decomposed into dimethylsilane, germane, hydrogen, and a germanium sub-

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(19) I. F. Kovalev, *Opt. Spectry.*, **6**, 387 (1959).

TABLE III
 INFRARED ABSORPTION BAND PEAKS AND ASSIGNMENTS^a

Vibration	(GeH ₃) ₄ Si	CH ₃ Si(GeH ₃) ₃	(CH ₃) ₂ Si(GeH ₃) ₂	(CH ₃) ₃ SiGeH ₃	(CH ₃) ₃ GeGeH ₃
$\nu_{\text{asym}}\text{CH}_3$		2970 w	2970 m	2978 s	2980 s
$\nu_{\text{sym}}\text{CH}_3$		2912 w	2900 w	2910 m	2915 s
νGeH_3	{ 2100 w 2072 vs 2000 w	{ 2115 m 2080 sh 2065 vs 2010 m	{ 2120 m 2065 s 2015 m	{ 2105 mw 2060 s 2010 mw	{ 2100 m 2055 vs 2010 m
$\delta_{\text{asym}}\text{CH}_3$		1410 w, b	1418 w	1412 w, br	1400 m
$\delta_{\text{sym}}\text{CH}_3$		1250 w	1258 m	{ 1262 s 1254 sh	1232 s
δGeH_3	{ 872 vw 772 vs	{ 885 m 768 vs	{ 883 s 765 vs 935 m, sh 883 s 840 sh	{ 786 s 850 vs 903 m 850 vs 781 s	{ 850 m, sh 772 vs 898 m, b 824 s
ρCH_3		802 m	810 vs	781 s	
$\nu_{\text{asym}}\text{Si-C}$			702 w	694 mw	
$\nu_{\text{sym}}\text{Si-C}$		693 w			

^a s, strong; medium; w, weak; v, very; br, broad; sh, shoulder.

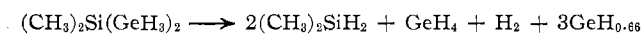
 TABLE IV
 PROTON NMR BAND POSITIONS

Compound	$\tau(\text{GeH})^a$	$\tau(\text{CH})^a$	Ratio of peak areas
(CH ₃) ₄ Si	...	10.49	...
(CH ₃) ₃ SiGeH ₃	7.42	9.97	1:3
(CH ₃) ₂ Si(GeH ₃) ₂	7.00	9.67	1:1
CH ₃ Si(GeH ₃) ₃	6.69	9.43	3:1
Si(GeH ₃) ₄	6.36
(CH ₃) ₄ Ge	...	9.87 ^b	...
(CH ₃) ₃ GeGeH ₃	7.07	9.75	1:3

^a Values in ppm for the neat liquid in capillary tubes compared with dilute TMS in CCl₄, τ 10.00 ppm, external standard.

^b Value for a dilute solution in CCl₄, from R. S. Drago and N. A. Matwiyoff, *J. Organometal. Chem.* (Amsterdam), **3**, 62 (1965).

hydride. From the amounts of products obtained, the stoichiometry of the reaction is given by



in which the germanium subhydride is assumed to have the empirical formula GeH_{0.66} in order to balance the equation. Compositions of this type are not unknown; for example, the pyrolysis of digermane²⁰ at 195–220° produced a germanium subhydride with composition GeH_{0.31}, and the pyrolysis of disilane gave a subhydride with the composition SiH_{0.7}. The actual composition of these subhydrides probably depends on the duration and temperature of pyrolysis.

The formation of dimethylsilane rather than digermysilane is not inconsistent with the fact that Si–Ge bonds are weaker than the Si–C bonds, as has recently been confirmed,^{21,22} assuming similar cleavage mechanisms.

Physical Properties.—As shown by the normal values of the Trouton constant (Table I), none of these compounds has a high degree of association in the liquid phase. This is expected because the molecules are probably only slightly polar, analogous to the unsubstituted hydrocarbons. The increase in the heat of

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vaporization, ΔH_v , is associated mainly with the increase in molecular weight as a methyl group is replaced by a germyl group.

Nmr Spectra.—Chemical shifts of the methyl and germyl protons of the methylgermysilanes (Table IV) decrease monotonically as the methyl groups are replaced by germyl groups. A similar decrease is observed for the methyl protons in the series (CH₃)_nMX_{4-n}, where M = C, Si, or Ge and X = H or Cl (except for (CH₃)_nCH_{4-n}, which give no change as *n* varies, and (CH₃)_nGeCl_{4-n}, which have not yet been measured), as methyl groups are replaced by hydrogen or chlorine atoms.^{23–26} This decrease can be qualitatively attributed to an inductive effect as methyl groups are replaced by more electronegative chlorine atoms or protons.²⁷ Such an explanation, however, is not applicable to the methylgermysilanes. Since it is reasonable to assume that the electronegativity of the germyl group is less than that of the methyl group, the inductive effect should cause an increase in the proton chemical shifts as the methyl groups are replaced by germyl groups. The apparently anomalous shift observed can be explained in terms of the magnetic anisotropy, which includes the dispersion effect,^{28,29} of the Si–C and Si–Ge bonds. Since the germyl group is much larger than the methyl group, the anisotropic effect should cause a decrease in the proton chemical shift as the methyl groups are replaced by germyl groups. In order to account for the observed changes in the chemical shift, it is necessary to assume that the anisotropic effect predominates over the inductive effect.

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