tion is probably due to the formation of di- and trisubstituted borazines which decompose more readily than the monosubstituted derivative. The formation of polysubstituted borazines is indicated from the observation that alcohol was always consumed faster than borazine even when the initial alcohol to borazine ratio was greater than unity.

The most abundant ions produced by fragmentation in the mass spectrum of borazine are $B_3N_3H_5^+$, $B_3N_2H_2^+$, $B_2N_2H_3^+$, $B_2NH_2^+$, and BNH_3^+.[7] In the mass spectrum of B-monomethoxy- and B-monoethoxyborazine major ion fragments occur in positions corresponding to the base groups in borazine shifted to higher masses due to the substitution of an alkoxy group for an H atom. Ion fragments in the alkoxy derivatives also arise by splitting off segments of the side chain.

[7] American Petroleum Institute Research Project 44, Mass Spectral Data, Serial No. 1346.

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The Preparation of Methylsilyl Methyl Ether and a Base Strength Study of the Monomethoxy Derivatives of Methylsilane

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There have been very few investigations reported in the literature which compare the carbon functional and silicon functional isomers of CH_3SiH_3.[1-3] In a recent report, Varma has described the preparation and properties of the first carbon-substituted methoxy derivative of CH_3SiH_3, *i.e.*, $CH_3OCH_2SiH_3$.[4] The present investigation was undertaken to prepare and characterize the silicon-substituted isomer, $CH_3OSiH_2CH_3$, and to investigate the Lewis basicities of the two compounds.

Experimental Section

General Methods.—A conventional Pyrex-glass high-vacuum system was used to manipulate all volatile materials. Mass spectra (at 70 v) were obtained by means of a Consolidated Electrodynamics mass spectrometer, Model 21-103C. Infrared absorption spectra were recorded with a Perkin-Elmer 137B infracord spectrophotometer on the gaseous phase at room temperature with the sample confined in a 10-cm cell fitted with KBr windows. Proton nuclear magnetic resonance data were obtained on a Varian Associates A-60 spectrometer operating at room temperature. The spectra were calibrated by the standard audiofrequency side-band interpolation technique. Gas chromatographic separations were performed on a slightly modified Varian-Aerograph Model A-90-P3 gas chromatograph equipped with a 20 ft × $^3/_8$ in aluminum column packed with 25% Carbowax 400 on Chromosorb W support (60–80 mesh). The unit was operated at a flow rate of 100 ml of He/min and at a column temperature of 30°. Infrared data on the hydrogen-bonding systems were obtained on a Beckman IR-9 spectrophotometer. Techniques employed for these measurements were identical with those previously reported.[5] Infrared spectra of the carbon tetrachloride–methanol (or phenol)–ether solutions (in an 0.08-mm cell) were taken for the silicon compounds studied after each base strength measurement in order to confirm their purity.

Materials.—$(CH_3SiH_2)_2S$ was prepared by passing CH_3SiH_2I over red HgS.[6] Analytical grade CH_3OH was dried over BaO and distilled in the vacuum line. $CH_3OCH_2SiH_3$ was prepared by allowing $ClCH_2OCH_3$ to react with solid $KSiH_3$.[4] The $CH_3OCH_2SiH_3$ could not be completely purified in the vacuum line and was purified by gas chromatographic techniques (retention time was 12.5 min; vapor pressure at $-47.8°$ was found to be 16.8 mm; lit.,[4] 16.1 mm; confirmed by infrared spectrum[4]). $CH_3OCH_2CH_3$ was prepared by allowing $NaOCH_3$ to react with CH_3CH_2Br. The product was purified by vapor-phase chromatography (retention time, 9.5 min; identity and purity confirmed by its infrared spectrum[7]). Phenol was purified by sublimation *in vacuo*.

Synthesis of $CH_3OSiH_2CH_3$.—$(CH_3SiH_2)_2S$ (4.88 mmoles) and CH_3OH (9.28 mmoles) were combined and allowed to react at room temperature for approximately 5 min. No noncondensable material (at $-196°$) was produced in the reaction. Distillation of the products through a series of traps held at -112, -134, and $-196°$ yielded pure $CH_3OSiH_2CH_3$ (*ca.* 8.7 mmoles, 94% yield; mol wt found 76.3, calcd 76.18) as a condensate in the $-134°$ trap. H_2S (4.34 mmoles; mol wt found 33.8, calcd 34.08) collected in the $-196°$ trap.

Anal.[8] Calcd for C_2H_8SiO: C, 31.54; H, 10.59; Si, 36.87. Found: C, 31.83; H, 10.57; Si, 36.78.

Infrared, Nmr, and Mass Spectra.—The absorption maxima in the infrared spectrum of $CH_3OSiH_2CH_3$ (pressure ~10 mm) are (in cm^{-1}): 2941 (w), 2809 (w), 2123 (s), {1261, 1245 (w)} d, 1188 (w), 1100 (s), 966 (sh), {942, 932 (vs)} d, 927 (sh), 864 (w), 758 (m).

The proton nuclear magnetic resonance spectrum (τ) of $CH_3OSiH_2CH_3$ (20% by volume in cyclohexane, τ(cyclohexane) 8.56) consisted of an unresolvable singlet at 6.58 (±0.01) (CH_3O protons), a 1:2:1 triplet at 9.77 (±0.01) (CH_3Si protons), and a 1:3:3:1 quartet at 5.44 (±0.01) (SiH_2 protons). Other data obtained from the spectrum: $J_{H-H'} = 3.0$ cps and $J_{^{29}Si-H} = 207.6$ cps.

The mass spectrum of $CH_3OSiH_2CH_3$ is consistent with its proposed structure. Possible assignments of the major fragments observed are (*m/e*, ion, relative intensity): 76, C_2H_8SiO, 10.3; 75, C_2H_7SiO, 100.0; 61, CH_5SiO, 43.8; 59, CH_3SiO, 26.7; 45, CH_5Si and HSiO, 56.4; 31, CH_3O, 13.3; 15, CH_3, 13.4.

Vapor Pressure and Melting Point.—The vapor pressures of a freshly purified sample of $CH_3OSiH_2CH_3$ at a number of temperatures are listed in Table I. The inner surface of the manometer was pretreated with a separate sample of $CH_3OSiH_2CH_3$. Vapor pressures in the range -74.3 to $-32.4°$ are given by

$$\log P_{\text{mm}} = \frac{-1487.7}{t + 273.16} + 8.1956$$

which gives an extrapolated boiling point of $+6.8°$, a molar heat of vaporization of 6807.6 cal, and a Trouton constant of 24.3 cal deg^{-1} $mole^{-1}$.

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TABLE I

VAPOR PRESSURES OF $CH_3OSiH_2CH_3$[a,c]

Temp, °C	P, mm Obsd	P, mm Calcd	Temp, °C	P, mm Obsd	P, mm Calcd
−74.3	5.2	5.2	−36.6	80.3	80.7
−68.6	8.5	8.4	−34.6	90.6	91.1
−63.8	12.6	12.3	−32.4	101.4	103.9
−60.0	16.8	16.5	−38.3[b]	72.2	72.6
−49.6	35.1	34.8	−43.4[b]	53.4	52.6
−44.6	49.0	48.6	−64.0[b]	12.5	12.1
			−196[b]	0.0	. . .

[a] Duration of the experiment approximately 8 hr. [b] Pressure observed on decreasing the temperature. [c] The molecular weight of the sample at the conclusion of the experiment was 76.5 (calcd 76.18); the infrared spectrum was identical with that of the pure material.

The melting point of $CH_3OSiH_2CH_3$, determined by using a Stock magnetic plunger apparatus,[9] was −140.0 ± 0.2°.

Results and Discussion

The new methoxy derivative of CH_3SiH_3, methylsilyl methyl ether, $CH_3OSiH_2CH_3$, has been prepared in good yield by the reaction of CH_3OH with $(CH_3SiH_2)_2S$ at room temperature.

$$2CH_3OH + (CH_3SiH_2)_2S \longrightarrow 2CH_3OSiH_2CH_3 + H_2S \quad (1)$$

The structure of the compound was confirmed by its mass, infrared, and proton nuclear magnetic resonance spectra.

It is of interest to note that the boiling point of the silicon-substituted compound $CH_3OSiH_2CH_3$ (+6.8°) is considerably lower than the boiling point of the isomeric carbon-substituted compound $CH_3OCH_2SiH_3$ (+25.0°).[4] The boiling points of the isomeric halide derivatives of CH_3SiH_3 (Cl, Br, I) are also in this same relative order.[10,11] For these latter derivatives, this trend cannot be attributed to a molecular polarity effect, since the dipole moments of the silicon-substituted compounds are greater than the dipole moments of the analogous carbon-substituted compounds.[12] Dipole moment data are not available for the CH_3O isomers, but presumably a similar situation exists.

The proton nmr spectrum of $CH_3OSiH_2CH_3$ in cyclohexane was analyzed as a first-order system. The general features of the spectrum are identical with those observed for other monomethylsilyl derivatives.[13] No long-range proton coupling was observed. The compound can readily be distinguished from its carbon-substituted isomer by an examination of the ^{29}Si satellites. As expected, the ^{29}Si satellites of $CH_3OSiH_2CH_3$ are 1:3:3:1 quartets, whereas for $CH_3OCH_2SiH_3$ they are basically 1:2:1 triplets.[4] The "C–Si bond shift" of $CH_3OSiH_2CH_3$ is calculated to be 0.04 ppm.[13] Adding this quantity to $\tau(CH_3SiH_2)$ gives the characteristic "constant" (9.81) which has been observed for other monomethylsilyl compounds.[13,14] The significance of this "constant" has been discussed elsewhere.[13] The calculated $J_{^{29}Si-H}$ coupling constant[13] for $CH_3OSiH_2CH_3$ (207.9 cps) agrees quite well with the experimental value (207.6 cps).

It is of interest to note that the CH_3O chemical shifts of CH_3OSiH_3 and $CH_3OSiH_2CH_3$ are essentially identical[14] and are positioned at a lower field than the CH_3O protons in $(CH_3)_2O$ and $CH_3OCH_2SiH_3$.[15,16] A similar low-field position has been reported for the chemical shift of the CH_3O protons in $CH_3OSi(CH_3)_3$ relative to the chemical shift of the CH_3O protons in $CH_3OC(CH_3)_3$.[17] This order is opposite to that predicted from simple electronegativity effects, since the electronegativity of silicon is less than that of carbon.[18] The apparent anomaly has been attributed to (p→d) π bonding in the Si–O linkage.[17] Although we do not rule out the existence of π bonding in the Si–O linkage, we do not believe that it is the main reason for the low-field position of the CH_3O protons in these alkoxysilanes. This conclusion is based on the fact that although the electronegativity values of silicon and germanium are approximately the same,[18] the CH_3O chemical shifts of methoxygermanes also fall at unexpectedly low fields relative to the CH_3O chemical shifts of analogous carbon ethers[19,20] and (p→d) π bonding has been shown to be much less important in the Ge–O linkage than it is in the Si–O linkage.[21-23] The fallibility of interpreting chemical shift data in terms of electronegativity and π-bonding considerations has previously been pointed out by Ebsworth and Frankiss.[24] Anisotropy and dispersion effects have not been fully investigated for compounds of this type and may offer a satisfactory explanation for this behavior.[25-27]

An infrared hydrogen-bonding study of the interaction of $CH_3OCH_2SiH_3$, $CH_3OSiH_2CH_3$, and $CH_3OCH_2CH_3$ with phenol and/or methanol was carried out in order to investigate the relative Lewis basicities of the various ethers. The shift ($\Delta\nu_{OH}$) of the 3610-cm^{-1} band of phenol and/or the 3643-cm^{-1} band of methanol upon complexation with the ethers was taken as a measure of the hydrogen-bonding interaction. It has been well established that the ether which shows a greater value of $\Delta\nu$ with a given refer-

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ence alcohol is the stronger base.[5,28–30] Methanol was chosen as the reference acid for CH_3OSiH_3 and $CH_3OSiH_2CH_3$ since phenol has previously been found to undergo a rapid reaction with compounds of this type.[31] Data for the isomers and other systems of interest are listed in Table II.

TABLE II

METHANOL AND PHENOL FREQUENCY SHIFT DATA[a]

Ether	Ether concn, M	$\Delta\nu_{OH}$ Methanol	Phenol
CH_3OCH_3[b]	0.25	128	251
$CH_3OCH_2CH_3$	0.12	142	268
$CH_3OCH_2SiH_3$	0.12	*d*	246
CH_3OSiH_3[c]	0.25	92	183[e]
$CH_3OSiH_2CH_3$	0.12	114	221[e]

[a] Solvent, CCl_4; concentrations: phenol, 0.005 M; methanol, 0.01 M; values reproducible to ± 3 cm^{-1}. [b] Reference 5. [c] Reference 31. [d] No hydrogen-bonded OH absorption observed. [e] Values extrapolated from methanol data. Phenol frequency shifts (± 4 cm^{-1}) for a number of ethers are related to methanol frequency shifts by the relationship $\Delta\nu(\text{phenol}) = 1.76\Delta\nu(\text{methanol}) + 21.0$ (G. A. Gibbon, J. T. Wang, and C. H. Van Dyke, unpublished results).

The results indicate that when phenol is employed as reference acid, $CH_3OCH_2SiH_3$ acts as a stronger base than the silicon-substituted isomer $CH_3OSiH_2CH_3$. Although this behavior is not that predicted from simple electronegativity considerations, the results are in accord with other experimental observations that the donor properties of various mono- and dimethoxysilanes are less than their carbon analogs.[30,32] This has been attributed to (p→d) π bonding in the Si–O linkage.[1,2,30,32] The fact that no hydrogen-bonding interaction was observed between $CH_3OCH_2SiH_3$ and methanol cannot be explained at the present time. Weak intermolecular association of the $CH_3OCH_2SiH_3$ (broken up when phenol is employed as reference acid) could be responsible for this, although in dilute solutions association should not be very important. In addition, no appreciable association of pure $CH_3OCH_2SiH_3$ has been reported.[4]

The observation that $CH_3OSiH_2CH_3$ is a stronger base than CH_3OSiH_3 can be attributed to the well-known electron-releasing characteristics ($+I$ effect) of the CH_3 group.[33] The relative basicities of $(CH_3)_2O$ and $CH_3OCH_2CH_3$ also reflect this $+I$ effect. It also appears that the CH_3 group is more electron releasing through the SiH_2 group than it is through the CH_2 group.

It is of particular interest to note that in the present hydrogen-bonding study $CH_3OCH_2SiH_3$ acts as a weaker base than $CH_3OCH_2CH_3$. This indicates that to a CH_2 group in these ether systems, the CH_3 group is more electron releasing than the SiH_3 group. This is also contrary to simple electronegativity considerations. It is unlikely that steric factors are responsible for this behavior, since the steric requirements for methanol and phenol in hydrogen-bond formation are low.[5,30] Recently, evidence has been gathered which points to a possible interaction between the unshared electrons of a potential donor atom, *e.g.*, Cl or N, and the d orbitals of silicon through an intervening CH_2 group.[12,34] The effect of this interaction in the case of ethers with $-OCH_2Si-$ linkages would be to reduce their Lewis basicity relative to ethers where such an interaction is not possible. The base strength data which we have obtained are in agreement with such a postulate. However, before definite conclusions can be drawn, further work on this general topic needs to be done.

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Substitution Reactions of Oxalato Complex Ions. VII. Inert Salt Effects on the Acid-Catalyzed Aquation of Tris(oxalato)chromium(III) Anion[1]

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In an earlier study[2] of the acid-catalyzed aquation of the tris(oxalato)chromium(III) anion, the kinetics were evaluated at constant ionic strength ($I = 1.0$). The rate studies, which included deuterium solvent isotope effect experiments, led to the conclusion that the reaction took place by the following dual-path mechanism: (a) Rapid protonation–dechelation equilibration

$$\mathrm{Cr(C_2O_4)_3^{3-} + H_3O^+ \rightleftharpoons Cr(C_2O_4)_2\cdot OC_2O_3H\cdot OH_2^{2-}},\quad K \tag{1}$$

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