TABLE VI
INTERATOMIC DISTANCES (Å) IN Li_4RhH_5

Rh–Rh	3.88	Li(2)–2 Rh	2.79
–4 Li(1)	2.55	–Li(1)	2.56
–4 Li(2)	2.79	–2 Li(1)	2.71
–2 H(1)	1.81	–2 Li(1)	2.75
–2 H(2)	1.95	–Li (2)	2.67
–2 H(3)	1.96	–2 H(1)	1.83
Li(1)–2 Rh	2.55	–2 H(2)	1.94
–Li(1)	2.46	–H(3)	1.82
–Li(1)	2.53	H(1)–Rh	1.81
–Li(2)	2.56	–2 Li(1)	1.95
–2 Li(2)	2.71	–2 Li(2)	1.83
–Li(2)	2.75	–H(1)	2.16
–2 H(1)	1.95	H(2)–Rh	1.95
–H(2)	1.95	–Li(1)	1.95
–H(2)	1.97	–Li(1)	1.97
–H(3)	1.82	–2 Li(2)	1.94
		H(3)–2 Rh	1.96
		–2 Li(1)	1.82
		–2 Li(2)	1.82

found in tris(triphenylphosphine)rhodium carbonyl hydride.[12]

The similarities between the proposed structures and Li–H distances for the lithium–rhodium hydrides and those of lithium hydride, along with other similarities such as brittleness and reaction with water to yield hydrogen gas, lead to the conclusion that the bonding of these compounds is predominantly ionic.

The fact that Li_4RhH_5 exhibits temperature-independent paramagnetism is consistent with an ionic model. The temperature-independent paramagnetism of Li_4RhH_4 is suggestive of rhodium metallic bonding along the *c* axis of the crystal. Preliminary room-temperature electrical resistivity measurements on polycrystalline samples (resistivities of about 0.5 ohm cm for Li_4RhH_4 and about 1.5 ohm cm for Li_4RhH_5) are inconclusive on this point, but the relatively large Rh–Rh distance (4.11 Å) along the *c* axis argues against delocalized metallic bonding between rhodium atoms. On the other hand, intermetallic bonding between rhodium and lithium is quite possible. The Li–Rh interatomic distances in both compounds are similar to that found in the intermetallic compound LiRh (2.663 Å).[13] This type of bonding may account for the apparent absence of an unpaired electron in the four-hydrogen compound.

In conclusion it should be noted that the lithium rhodium hydrides are not unique. We are currently studying the Li–Pd–H and Li–Ir–H systems and find evidence of ternary hydrides.[14,15] Graefe and Robeson[16] have observed reactions between lithium hydride and several metals. Moyer, *et al.*,[17] have prepared and studied Sr_2IrH_4 and in addition have observed ternary phases in other alkaline earth–transition metal–hydrogen systems. Reilly and Wiswall[18] have studied the properties of Mg_2NiH_4, which they prepared by hydriding Mg_2Ni. There are obvious similarities between these compounds, and one naturally seeks a unifying concept to account for their bonding and structures. We hope that the structures proposed here for the lithium rhodium hydrides and the ionic model deduced therefrom will help in attaining that goal.

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The Use of Phosphorus Pentafluoride as a Fluorinating Agent in Organosilicon Chemistry. III.[1] Synthesis and Characterization of Some New Fluorosiloxanes[2]

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Although the silicon–oxygen bond of siloxanes and alkoxysilanes is readily cleaved by phosphorus pentafluoride, the silicon–hydrogen bond of hydrosiloxanes can be easily fluorinated at low temperatures by this reagent thus providing a convenient source of fluorosiloxanes. The synthesis and characterization of $FSiH_2OSiH_3$, $(FSiH_2)_2O$, $F(CH_3)HSiOSiH_2CH_3$, and $[F(CH_3)HSi]_2O$ are described.

Introduction

In the course of investigating the cleavage of the silicon–oxygen bond of siloxanes by phosphorus pentafluoride, we observed an interesting fluorination reaction occurring with siloxanes that contained silicon–hydrogen bonds.[1a] Fluorosiloxanes were produced in the reaction together with the expected cleavage products. Since methods of preparing partially fluorinated siloxanes are practically nonexistent, we undertook a study into the general feasibility of preparing these types of compounds by the interaction of hydrosiloxanes with phosphorus pentafluoride.

Experimental Section

Apparatus.—A conventional Pyrex-glass high-vacuum system

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was used to manipulate all volatile compounds.[3] Stopcocks and ground-glass joints were lubricated with Apiezon N grease. Mass spectra were obtained by means of an AEI Model MS-9 mass spectrometer. 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 Hitachi Perkin-Elmer R20 spectrometer operating at ambient temperatures. Sample concentrations were approximately 10–15% by volume in $CFCl_3$ with a small amount of $(CH_3)_4Si$ added as an internal reference.

Gas chromatographic separations were performed on a modified Varian Aerograph Model A-90-P3 gas chromatograph equipped with an 18 ft × $^3/_8$ in. aluminum column packed with a 20% silicone oil (710) on Chromosorb W (60–80 mesh) support. A special inlet and collection system was constructed which allowed the samples to be chromatographed without exposure to air. The unit was operated at a flow rate of 100 cm^3 of He min^{-1} and at a column temperature of 30°. All reactions were carried out in 15-ml all-glass break-seal tubes.

Materials.—PF_5 (Air Products) was purified by repeated distillations through a trap at $-134°$ and characterized by its infrared spectrum.[4] $(SiH_3)_2O$ (mol wt: calcd, 78.2; found, 77.7; purity confirmed by its infrared spectrum[5]) was prepared by the hydrolysis of SiH_3Br and purified by distillations through a trap at $-111°$. $(CH_3SiH_2)_2O$ (mol wt: calcd, 106.3; found, 106.1; purity confirmed by its infrared spectrum[6]) was prepared by the hydrolysis of $(CH_3SiH_2)_2S$.[7] CH_3OSiH_3 (mol wt: calcd, 62.2; found, 62.3; purity confirmed by its infrared spectrum[8,9]) and $CH_3OSi(CH_3)_3$ (mol wt: calcd, 104.2; found, 105.1; purity confirmed by gas chromatography) were prepared by the interaction of CH_3OH with $(SiH_3)_2S$ and $[(CH_3)_3Si]_2S$, respectively.[9,10] $(SiH_3)_2S$, $(CH_3SiH_2)_2S$, and $[(CH_3)_3Si]_2S$ were prepared by interacting the corresponding iodosilane with HgS.[7,11,12] Samples of SiH_3Br and $(Si_2H_5)_2O$ were kindly provided by Dr. L. G. L. Ward. $[(CH_3)_3Si]_2O$ (Anderson; purity confirmed by its infrared spectrum[13]) was purified by distillation in the vacuum line.

Syntheses. $FSiH_2OSiH_3$.—The interaction of $(SiH_3)_2O$ (2.0 mmol) with PF_5 (2.1 mmol) at $-78°$ for 15 min produces a mixture of the new fluorosiloxanes $FSiH_2OSiH_3$ and $(FSiH_2)_2O$ (identified by mass spectroscopy) together with various other compounds including POF_3, PF_3, SiH_3F, SiH_2F_2, and SiF_4, all of which can be identified by their characteristic infrared spectra.[14-18] Hydrogen is also produced in the reaction and can be removed from the products by its distillation through a $-196°$ trap. The fluorosiloxanes can be removed with POF_3 as an impurity from the product mixture by their condensation in a trap at $-134°$. Impure $FSiH_2OSiH_3$ is recovered by passing the condensate through a trap at $-116°$, in which most of the $(FSiH_2)_2O$ and POF_3 condense. Small amounts of $(FSiH_2)_2O$ and POF_3 do pass the trap at $-116°$ and the final purification of $FSiH_2OSiH_3$ in this work was achieved by gas chromatography [compound (retention time, min): POF_3 (3.8), $FSiH_2OSiH_3$ (4.5), $(FSiH_2)_2O$ (4.8)]. Care must be taken in order to obtain $FSiH_2OSiH_3$ free of $(FSiH_2)_2O$, owing to the closeness of their retention times. To separate the latter two compounds, it was necessary to divert the effluent from the chromatograph from the trap collecting the $FSiH_2OSiH_3$ before the $(FSiH_2)_2O$ began to appear. This resulted in some loss of $FSiH_2OSiH_3$, due to the overlap of peaks, although the total yield of $FSiH_2OSiH_3$ (1.2 mmol) in the reaction described was 60%. The purity of the compound was confirmed by its gas-phase molecular weight (calcd 96.2, found 96.2) and by its mass and proton nmr spectra. The proton nmr spectrum consists of a singlet and a widely spaced doublet in a 3:2 ratio, assigned to the SiH_3 and SiH_2F protons, respectively. On further scale expansion, the singlet absorption was actually a closely spaced doublet, owing to long-range F–H coupling. Data are given in the Discussion.

$FSiH_2OSiH_3$, when purified, can be manipulated in standard vacuum-line operations without any decomposition. It does not react with mercury or glass.

$(FSiH_2)_2O$.—A reaction identical with the one used to synthesize $FSiH_2OSiH_3$ can be used to prepare $(FSiH_2)_2O$, although better yields are obtained if the ratio of PF_5 to $(SiH_3)_2O$ is increased and a longer reaction time is employed. As an illustration, $(SiH_3)_2O$ (2.0 mmol) and PF_5 (4.2 mmol) were allowed to interact at $-78°$ for 1 hr. Hydrogen is removed as described previously. Both $(FSiH_2)_2O$ and POF_3 condense in a trap at $-116°$, while the other products formed are sufficiently volatile at this temperature to pass through. The final purification of $(FSiH_2)_2O$ (0.62 mmol, 31% yield) was achieved by gas chromatography [compound (retention time, min): $(FSiH_2)_2O$ (4.8), POF_3 (3.8)]. The purity of the $(FSiH_2)_2O$ was confirmed by the compound's molecular weight (calcd 114.2, found 114.3) and mass spectrum. The single doublet proton nmr spectrum of the compound is consistent with the symmetrical $(FSiH_2)_2O$ formulation. Data are given in the Discussion. The compound does not react with mercury or glass and it can be manipulated in standard vacuum-line operations without any decomposition.

$CH_3SiHFOSiH_2CH_3$.—A typical synthesis of $CH_3SiHFOSiH_2CH_3$ involves allowing $(CH_3SiH_2)_2O$ (2.0 mmol) to react with PF_5 (2.0 mmol) at $-78°$ for 20 min. Hydrogen is removed and a mixture of the fluorosiloxanes $CH_3SiHFOSiH_2CH_3$ and $(CH_3SiHF)_2O$, together with POF_3, CH_3SiH_2F, and a small amount of $HPOF_2$ (last three compounds identified by their infrared spectra[6,14,19]), condenses in a $-134°$ trap while the more volatile products, PF_3 and SiF_4, pass through. Distillation of the $-134°$ condensate through a trap at $-96°$ removes $(CH_3SiHF)_2O$ and $HPOF_2$ while the $CH_3SiHFOSiH_2CH_3$ (1.15 mmol, 57% yield) is removed from the more volatile distillate by its subsequent condensation in a trap at $-111°$. The compound's purity was confirmed by its gas-phase molecular weight (calcd 124.3, found 124.7) and its mass spectrum. The proton nmr spectrum of $CH_3SiHFOSiH_2CH_3$ consisted of three quartets, two doublets, and one triplet, the relative intensities of which were in accord with the compound's structure. The data are presented in the Discussion. The compound can be distilled in the vacuum line without any decomposition.

$(CH_3SiHF)_2O$.—The synthesis of $(CH_3SiHF)_2O$ is readily achieved by interaction of $(CH_3SiH_2)_2O$ (2.0 mmol) with PF_5 (1.0 mmol) at $-78°$ for 30 min. $(CH_3SiHF)_2O$ and a small amount of $HPOF_2$ (identified by its infrared spectrum[19]) condense in a trap at $-96°$. The $HPOF_2$ can be removed from the $(CH_3SiHF)_2O$ by adding water to the mixture followed by additional fractionations. The purity of the $(CH_3SiHF)_2O$ (1.2 mmol, 60% yield) recovered was confirmed by its gas-phase molecular weight (calcd 142.3, found 141.7) and its mass spectrum. The proton nmr spectrum of the compound has been reported previously and is consistent with the symmetrical $(CH_3SiHF)_2O$ formulation.[20]

Mass Spectra of $FSiH_2OSiH_3$, $(FSiH_2)_2O$, $CH_3SiHFOSiH_2CH_3$, and $(CH_3SiHF)_2O$.—The parent ion and the expected fragments were observed in the 70-eV mass spectra of the fluorosiloxanes. In each instance the parent ion less one hydrogen (P − 1 fragment) was the most intense peak in the spectrum. Precise mass measurements for the P − 1 fragments yielded the following data (fragment, precise mass, calculated mass): $^{28}Si_2H_4FO^+$, 94.9787, 94.9785; $^{28}Si_2H_3F_2O^+$, 112.9692, 112.9691; $^{28}Si_2C_2H_8FO^+$, 123.0100, 123.0098; $^{28}Si_2C_2H_7F_2O^+$, 141.0004, 141.0004.

Vapor Pressures of $FSiH_2OSiH_3$, $(FSiH_2)_2O$, and $CH_3SiHFOSiH_2CH_3$.—The vapor pressures of freshly purified samples were measured at a number of temperatures in a pretreated mercury manometer system. Data were obtained with both

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ascending and descending temperatures to check reproducibility and to detect decomposition during the measurements. The results are given in Table I.

TABLE I

VAPOR PRESSURE DATA FOR THE NEW FLUOROSILOXANES

$FSiH_2OSiH_3$			$(FSiH_2)_2O$			$CH_3SiHFOSiH_2CH_3$		
Temp, °C	P, Torr Calcd	P, Torr Obsd	Temp, °C	P, Torr Calcd	P, Torr Obsd	Temp, °C	P, Torr Calcd	P, Torr Obsd
−96.2	4.7	4.7	−95.8	8.0	8.2	−78.0	2.5	2.8
−86.6	10.3	10.3	−84.1	16.4	16.0	−64.0	6.3	5.8
−80.9	15.8	16.0	−77.9	23.2	22.7	−55.8	10.1	9.6
−78.9	18.2	18.5	−73.2	29.8	29.4	−47.9	15.5	15.0
−70.7	32.0	31.9	−64.0	47.1	47.3	−36.2	27.7	27.8
−67.8	38.6	38.7	−61.7	52.4	52.7	−23.8	48.3	49.5
−64.2	48.5	49.0	−55.1	70.6	71.1	−36.3[a]	27.6	27.7
−55.0	83.6	83.8	−51.0	84.1	85.0	−47.9[a]	15.5	15.0
−45.1	143.0	142.9	−64.0[a]	47.1	47.4	−55.8[a]	10.1	9.6
−64.2[a]	48.5	49.1	−77.9[a]	23.2	22.8	−64.1[a]	6.3	6.0
−78.9[a]	18.2	18.5	−95.8[a]	8.0	8.2			
−96.2[a]	4.7	4.7						

[a] Pressure observed on decreasing the temperature.

Vapor pressures in the ranges studied are given by the following equations: For $FSiH_2OSiH_3$

$$\log P_{\text{Torr}} = \frac{-1172.5}{t + 273.16} + 7.2965$$

for $(FSiH_2)_2O$

$$\log P_{\text{Torr}} = \frac{-901.2}{t + 273.16} + 5.9814$$

and for $CH_3SiHFOSiH_2CH_3$

$$\log P_{\text{Torr}} = \frac{-1148.4}{t + 273.16} + 6.2892$$

Extrapolated boiling points are −7.6° for $FSiH_2OSiH_3$, 17.5° for $(FSiH_2)_2O$, and 63.8° for $CH_3SiHFOSiH_2CH_3$.

Infrared Spectra of $FSiH_2OSiH_3$, $(FSiH_2)_2O$, $CH_3SiHFOSiH_2CH_3$, and $(CH_3SiHF)_2O$.—Gas-phase infrared absorption data for the above fluorosiloxanes are summarized together with tentative assignments of the bands in Tables II and III.

TABLE II

INFRARED ABSORPTION MAXIMA OF $FSiH_2OSiH_3$ AND $(FSiH_2)_2O$

$FSiH_2OSiH_3$[a]	$(FSiH_2)_2O$[b]	Assignment[c]
2207 s	2212	Si–H str
1720 w	1740 w	Combination of sym and asym Si–O–Si str
1225 w	1230 w	Combination of Si–O str (asym) and Si–O–Si skeletal bend mode[d]
1123 s	1134 s	Si–O–Si str (asym)
970 s	978 s	Bend of the SiH_2 angles
948 936 d, vs	937 927 d, vs	Si–F str
883 868 d, w	883 872 d, m	Unassigned
731 m	723 m	SiH_3 and/or SiH_2 rock (or twist)

[a] Spectrum recorded at pressures of 3 and 9 Torr. [b] Spectrum recorded at pressures of 3 and 8 Torr. [c] Tentative assignments for the absorptions made by comparing the spectra with the assigned spectra of $(SiH_3)_2O$,[5] SiH_3F,[16] and CH_3SiH_2F.[6] [d] $\nu_{\text{Si-O(asym)}} + 2\delta_{\text{Si-O-Si}}$.

Reactions of Phosphorus Pentafluoride. (a) **With Hexamethyldisiloxane.**—The reaction of $[(CH_3)_3Si]_2O$ (1.0 mmol) with PF_5 (1.0 mmol) at 25° for 1 hr produced a mixture of $(CH_3)_3SiF$ (2.0 mmol) and POF_3 (1.0 mmol). The components of the mixture could not be quantitatively separated by standard vacuum line fractionations; the analysis was made by mixed molecular weight data, gas chromatography, and the infrared spectra of the compounds.[14,21] No reaction was observed on holding a mixture of $[(CH_3)_3Si]_2O$ (1.6 mmol) with PF_5 (1.0 mmol) at −78° for 24 hr.

TABLE III

INFRARED ABSORPTION MAXIMA OF $CH_3SiHFOSiH_2CH_3$ AND $(CH_3SiHF)_2O$

$CH_3SiHFOSiH_2CH_3$[a]	$(CH_3SiHF)_2O$[b]	Assignment[c]
2973 m	2989	C–H str
2196 2161 d, s	2202 s	Si–H str
1672 w	1685 w	Combination of sym and asym Si–O–Si str
1405 w	1405 1381 d, w	CH_3 def (asym)
1266 m	1271 m	CH_3 def (sym)
1180 w	1183 w	Unassigned
1102 s	1115 s	Si–O–Si str (asym)
957 s	931 s	SiH and SiH_2 bend (scissors)
918 sh		
900 s	889 s	Si–F str
845 w	843 m	CH_3 rock
771 s	773 s	Si–C str
510 w		SiH_2 rock

[a] Spectrum recorded at pressures of 4 and 13 Torr. [b] Spectrum recorded at pressures of 6 and 12 Torr. [c] Tentative assignments for the absorptions made by comparing the spectra with the assigned spectra of $(CH_3SiH_2)_2O$ and CH_3SiH_2F.[6]

(b) **With Methoxytrimethylsilane.**—The 12-hr reaction of $CH_3OSi(CH_3)_3$ (1.0 mmol) with PF_5 (1.0 mmol) at room temperature produced a white solid and $(CH_3)_3SiF$ (1.0 mmol, confirmed by its infrared spectrum[21]), together with small amounts of several other volatile products identified by their mass or infrared spectra as CH_3F, POF_3, and CH_3OPOF_2.[14,22]

(c) **With Methoxysilane.**—The 12-hr reaction of CH_3OSiH_3 (1.0 mmol) and PF_5 (1.0 mmol) at −78° produced a nonvolatile white solid and SiH_3F (1.0 mmol) (mol wt: calcd, 50.1; found, 49.7; confirmed by its infrared spectrum[16]) together with a small amount of CH_3OPOF_2. There was a trace amount of hydrogen produced in the reaction; PF_3 and POF_3 were not formed. The solid material decomposed to form an uncharacterized oily liquid after several hours at room temperature.

The reaction was repeated using approximately 1:1.4 and 1:2.5 mole ratios of PF_5 to CH_3OSiH_3. In each case, a white solid formed together with SiH_3F (1.3 and 1.7 mmol in each case, respectively) and trace amounts of other compounds as described above.

(d) **With Bis(disilanyl) Ether.**—A mixture of PF_5 (0.36 mmol) and $(SiH_3SiH_2)_2O$ (0.35 mmol) was held at −78° for 1 hr. The products could not be completely separated in the vacuum line but were separated into SiH_3SiH_2F (0.7 mmol identified by its infrared spectrum[23]) and POF_3 (0.36 mmol identified by its infrared spectrum[14]) by gas chromatography.

(e) **Attempted Reaction with Disilyl Sulfide.**—A mixture of $(SiH_3)_2S$ (2.0 mmol) and PF_5 (2.0 mmol) was held at −78° for 12 hr. There were no signs of a reaction occurring under these conditions, based on distillation and infrared data.[4,24] Similarly, after 3 hr at −45° and after 6 hr at room temperature, there was no sign of a reaction occurring. At the end of these experiments, $(SiH_3)_2S$ (1.99 mmol), PF_5 (1.96 mmol), and a trace amount of POF_3 were recovered from the final reaction tube.

Results and Discussion

Having shown that phosphorus pentafluoride readily fluorinates the silicon–hydrogen bond of siloxanes, we have undertaken a study of certain monomeric silicon compounds that contain silicon–hydrogen, silicon–fluorine, and silicon–oxygen bonds. Halosiloxanes have, of course, been reported in the literature, although very little work has been reported on fluorine-substituted siloxanes. The main synthesis of the few compounds of this type which have been reported is

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based on the hydrolysis of certain halofluorosilanes (halo = chloro, bromo, iodo). This method is successful owing to the greater tendency of silicon–chlorine, –bromine, or –iodine bonds to undergo hydrolysis than silicon–fluorine bonds. For example, polyorganofluorosiloxanes have been prepared by the hydrolysis of organofluorosilicon chlorides, $RSiCl_2F$.[25] The only organofluorosiloxane reported in the literature that contains silicon–hydrogen bonds is $(CH_3SiHF)_2O$. Frankiss has noted that this compound is formed as a side product in the antimony trifluoride conversion of CH_3SiHI_2 to CH_3SiHF_2 when a small amount of water is present.[20] Shortly after our work was completed, Britt and Moniz reported the synthesis of an organofluorosiloxane based on fluorination of the silicon–hydrogen bond in $[(CH_3)_3SiO]_2Si(H)CH_3$ by silver fluoride.[26]

We now report a convenient synthesis of certain monomeric fluorosiloxanes that is based on the fluorination of silicon–hydrogen bonds of hydrosiloxanes by phosphorus pentafluoride: $(RSiH_2)_2O + PF_5 \rightarrow RSiHFOSiH_2R + (RSiHF)_2O + HPF_4$ and/or H_2PF_3 ($R = CH_3$, H). The fluorophosphoranes presumably produced in the reaction were not isolated, owing to their facile decomposition in the vacuum line. Their known decomposition products in the presence of glass are H_2, PF_3, $HPOF_2$, and SiF_4, all of which were observed as products of the overall fluorination reactions.[27] These compounds are easily separated from fluorosiloxanes produced.

There are two competing reactions in the interaction of hydrosiloxanes with phosphorus pentafluoride. One involves the fluorination of the silicon–hydrogen bonds without cleaving the silicon–oxygen bonds, while the other is a straightforward Si–O–Si bond cleavage reaction that produces the corresponding silyl fluoride and POF_3. Phosphorus fluorides are known to cleave easily the silicon–oxygen bond of siloxanes,[28] and in order to fluorinate the silicon–hydrogen bond of hydrosiloxanes by our method, the reactions must be carried out at low temperatures. We found that −78° (Dry Ice bath) was a convenient temperature for fluorinating hydrosiloxanes by phosphorus pentafluoride. At higher temperatures, appreciable cleavage of the silicon–oxygen bond was noted. We have found that under these low-temperature conditions, phosphorus pentafluoride fluorinates only one silicon–hydrogen bond per silicon atom and that the reaction can be controlled to give the corresponding monofluoro or difluorodisiloxane by adjusting the duration of the reaction and in certain cases the relative amounts of reactants. We have tested the general fluorination reaction on $(SiH_3)_2O$ and $(CH_3SiH_2)_2O$ and have been able to prepare and characterize the fluorosiloxanes $FSiH_2OSiH_3$, $(FSiH_2)_2O$, $CH_3SiHFOSiH_2CH_3$, and $(CH_3SiHF)_2O$.

The mechanism for the siloxane fluorination reactions described has not been established although it is of interest to note some related fluorinations that involve phosphorus pentafluoride. This reagent is known to fluorinate the silicon–hydrogen bonds of certain other organosilicon compounds such as $CH_3SiH_2Co(CO)_4$, CH_3SiH_2Cl and various organosilanes at room temperature.[29] The interaction of organosilanes with phosphorus pentafluoride at 0° has been used to prepare organofluorosilicon hydrides of the type $RSiH_2F$ and $RSiHF_2$ (where $R = C_2H_5$, $CH_2{=}CH$, and $CH_3CH{=}CH_2$).[1b] In the present work, we found that hydrosiloxanes were fluorinated at much lower temperatures (−78°) than the other compounds which have been fluorinated by this method. Trichlorosilane is not fluorinated by phosphorus pentafluoride at room temperature, and, noting that the tendency to fluorinate the silicon–hydrogen bond increases in the series $Cl_3SiH < CH_3SiH_3 < (CH_3)_3SiH$, it has been suggested that the rate-controlling step in these reactions may involve an electrophilic attack of a silicon–hydrogen bond by phosphorus.[29]

Each of the fluorosiloxanes prepared gave first-order proton nmr spectra and the results were used to establish the symmetrical nature of the difluorodisiloxanes. A summary of the data obtained from the spectra together with data for the starting hydrosiloxanes is given in Table IV.

TABLE IV

PROTON MAGNETIC RESONANCE DATA FOR FLUOROSILOXANES AND RELATED SILICON ETHERS[a]

Compound	Proton environment	τ	$J_{^{29}Si-H}$	J_{HSiF}	Other coupling constants
$(CH_3SiH_2)_2O$[b]	CH_3	9.74	...	...	$J_{\overline{CHSiH}} = 3.3$
	SiH_2	5.33	212.3		
$CH'_3SiH'FOSiH_2CH_3$	CH'_3	9.74	...	...	$J_{\overline{CHSiH}} = 3.5$,
	CH_3	9.65	...	...	$J_{CH'SiH'} = 1.4$,
	SiH'	5.32	*e*	68.4	$J_{\overline{CH'SiH'F}} = 6.4$
	SiH_2	5.29	*e*	...	
$(CH_3SiHF)_2O$[c]	CH_3	9.70	...	...	$J_{\overline{CHSiH}} = 1.3$,
	SiH	5.26	261.1	68.2	$J_{\overline{CHSiHF}} = 6.6$
$(SiH_3)_2O$[d]	SiH_3	5.39	221.5	...	
SiH_3OSiH_2F	SiH_3	5.28	224.7	...	$J_{\overline{FSiOSiH}} = 0.5$
	$SiH_2(F)$	5.36	*e*	61.2	
$(SiH_2F)_2O$	$SiH_2(F)$	5.25	*e*	61.2	

[a] All coupling constants given in hertz. [b] E. A. V. Ebsworth and S. G. Frankiss, *Trans. Faraday Soc.*, **59**, 1518 (1963). [c] Reference 20. [d] E. A. V. Ebsworth and J. J. Turner, *J. Phys. Chem.*, **67**, 805 (1963); *J. Chem. Phys.* **36**, 2628 (1962). [e] Not observed.

In comparing the absorptions of the unsymmetrical siloxanes $FSiH_2OSiH_3$ and $CH_3SiHFOSiH_2CH_3$ with the corresponding starting hydrosiloxanes, it can be noted that the substitution of a fluorine for a hydrogen atom on silicon has caused only a very small downfield shift of the resonance due to the remaining proton(s) on that silicon atom but causes a larger downfield shift of the H(Si) absorption on the opposite side of the molecule. Similarly, in $CH_3SiHFOSiH_2CH_3$, the CH_3 protons on the unsubstituted silicon undergo more of a change than the CH_3 protons on the silicon atom where fluorine substitution has occurred. Unfortunately, the carbon analogs of the above silicon compounds have not been studied, thus preventing any comparisons along these lines. It is of particular interest to note, however, that this type of trend is not observed in comparing the chemical shift of $(CH_3)_2O$ (τ 6.79[30]) with

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

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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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