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Formation of Fluorosilylamines by the Interaction of Trisilylamine with Phosphorus Pentafluoride. Synthesis of 1,1'-Difluorotrisilylamine

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The selective halogenation of the silicon–hydrogen bond in hydrosilyl derivatives by inorganic halides has been shown to be a particularly good preparative method for obtaining a variety of specific halosilanes that may be difficult to prepare by other methods.[1,2] However at the present time it is by no means clear which hydrosilyl derivatives can be successfully halogenated by this method, particularly when the hydrosilyl derivative contains other reactive bonds. For example, PF_5 can be used to introduce silicon–fluorine bonds into $(SiH_3)_2O$ but not CH_3OSiH_3, $(Si_2H_5)_2O$, $(SiH_3)_2S$, or $(CF_3)_2PSiH_3$.[2,3] Tin(IV) chloride can be used to chlorinate partially the Si–H bonds of $(SiH_3)_3N$ but not $(SiH_3)_2O$.[4] In the present study, we have investigated the synthesis of fluorosilylamines by the interaction of $(SiH_3)_3N$ and $[HSi(CH_3)_2]_2NH$ with PF_5.

Experimental Section

Apparatus. A conventional Pyrex-glass high-vacuum system was used to manipulate all volatile compounds. Mass spectra were obtained at 70 eV on an AEI Model MS-9 mass spectrometer; infrared spectra were obtained on a Perkin-Elmer Model 457 spectrophotometer with the samples contained in a 10-cm gas cell fitted with KBr windows. Proton NMR spectra were obtained on a Hitachi Perkin-Elmer R-20 spectrometer operating at ambient temperature. Sample concentrations were approximately 5–10% by volume in cyclopentane, with a small amount of $(CH_3)_4Si$ added as an internal reference.

Materials. Trisilylamine and $[HSi(CH_3)_2]_2NH$ were prepared by the interaction of SiH_3Br and $HSi(CH_3)_2Cl$, respectively, with ammonia.[5] The purity of $[HSi(CH_3)_2]_2NH$ was checked by its gas-phase molecular weight (found 132.2, calcd 133.3) and infrared spectrum.[6] The purity of $(SiH_3)_3N$ was checked by its infrared[7] and mass spectra. Phosphorus pentafluoride was obtained commercially and purified on the vacuum line by its distillation through a trap at −134° (mol wt found 126.6, calcd 126.0; the infrared spectrum was identical with the published spectrum[8]).

Reactions of PF_5. (a) With Trisilylamine. $(SiH_3)_3N$ (1 mmol) and PF_5 (3 mmol) were condensed into an all-glass break-seal tube and allowed to react for 20 min at 0°. The volatile products were distilled through a trap maintained at −96° into a trap at −196°. An unidentified solid material remained in the reaction tube. The material in the −196° trap was identified as being a mixture of PF_3, SiH_3F, SiH_2F_2, and unreacted PF_5 by an infrared spectroscopic analysis.[8-11] The small amount of material in the −96° trap could not be conclusively identified by infrared spectroscopy, but a mass spectrum of the material clearly indicated the presence of $(SiH_3)_2NSiH_2F$, $SiH_3N(SiH_2F)_2$, and $N(SiH_2F)_3$, the majority of the sample being $SiH_3N(SiH_2F)_2$. Although the intensities of the parent ions of the fluorosilylamines were weak, the (parent − 1) peaks were strong and thus were used for obtaining precise mass measurements (ion, calculated mass, measured mass: Si_3H_7FN, 123.9870, 123.9886; $Si_3H_6F_2N$, 141.9776; 141.9782; $Si_3H_5F_3N$, 159.9682, 159.9674).

We repeated the reaction of $(SiH_3)_3N$ with PF_5 several times at different temperatures (−96 to 0°) and also by using different ratios of starting materials [1:1 and 6:1 mole ratios of PF_5:$(SiH_3)_3N$]. Fluorosilylamines were produced at temperatures between −50 and 0°, and it was observed that even when the mole ratios of starting materials were altered, the chief fluorosilylamine produced in most of the experiments was $SiH_3N(SiH_2F)_2$.

The fluorosilylamines produced in the above experiments could not be separated from one another by standard trap-to-trap vacuum-line fractionation techniques. Gas chromatography, using the equipment and columns available, also failed to purify the compounds. Partial success in separating the amines was achieved by using a low-temperature fractionating column similar to the one described by Jolly.[12] The materials subjected to this distillation were the combined −96° fractions obtained from the studies described above. Although the mass spectral results indicated that some $(SiH_3)_2NSiH_2F$ was present, we were not able to isolate any of this compound from the distillation. The bulk of the original sample was known to be $SiH_3N(SiH_2F)_2$ and we were able to obtain a sample of the pure difluoro derivative in the distillation. The experimental gas-phase molecular weight of the compound was 143.3 (calcd 144.4). A small amount of material believed to be $(FSiH_2)_3N$ from its proton NMR spectrum was also recovered. The yield of fluorosilylamines produced in any one reaction was usually small and did not exceed 5–10% overall.

(b) With 1,1,1',1'-Tetramethyldisilazane. Equimolar amounts (1.2 mmol) of PF_5 and $[HSi(CH_3)_2]NH$ were condensed into a glass reaction tube equipped with a vacuum Teflon stopcock and allowed to react for 45 min at −45°. The products were distilled through a −64° trap into a −196° trap. An infrared and mass spectral analysis revealed that the −64° trap contained unreacted $[HSi(CH_3)_2]_2NH$, while the −196° trap contained a mixture of PF_3, PF_5, $(CH_3)_2SiHF$, and $(CH_3)_2SiF_2$.[13] There was no mass spectral evidence of any fluorosilylamines in the products. The reaction was repeated at −78° for 10 min, after which time the previously cited distillation was repeated. Again, the −64° trap contained unreacted $[HSi(CH_3)_2]_2NH$ and the −196° trap contained the phosphorus and dimethylsilyl fluorides obtained in the initial reaction. We found no evidence of any fluorodimethylsilylamines in the reaction products.

Results and Discussion

At relatively low temperatures, the interaction of $(SiH_3)_3N$ with PF_5 proceeds along two pathways. The predominant reaction involves the cleavage of the silicon–nitrogen bond producing SiH_3F, while the second is an exchange reaction that results in the formation of fluorosilyl derivatives, i.e.

$$>N\text{-}SiH_3 + PF_5 \rightarrow >N\text{-}SiH_2F + [HPF_4]$$

The final form of the phosphorus-containing product in the cleavage reaction was not determined, and while we saw no direct evidence of fluorophosphoranes in the exchange reaction, the presence of PF_3 in the reaction products was confirmed and this compound is known to be one of the decomposition products of HPF_4 (or H_2PF_3), particularly in a glass vessel.[14] Precedence for the occurrence of both of these reactions involving PF_5 with silyl derivatives is available; for example both cleavage and hydrogen–fluorine exchange occur in the low-temperature reaction of $(SiH_3)_2O$ with PF_5.[2]

We were primarily interested in studying the fluorination reaction since it potentially offered a convenient synthesis of partially fluorinated silylamines. Mass spectral data unequivocally identified the presence of three fluorosilylamines in the volatile products of the fluorination reactions and this coupled with NMR data led us to identify the compounds as being $(SiH_3)_2NSiH_2F$, $SiH_3N(SiH_2F)_2$, and $(FSiH_2)_3N$. Although all three were detected in the reaction, for practical purposes only the difluoro compound could be conveniently synthesized by this procedure. Reaction conditions were altered to favor the formation of the monofluoro and the trifluoro derivatives by decreasing and increasing, respectively, the amount of PF_5 relative to $(SiH_3)_3N$ used in the reaction.

Table I. Infrared Absorption Frequencies of $(FSiH_2)_2NSiH_3$

Freq, cm^{-1}	Assignment[a]	Freq, cm^{-1}	Assignment[a]
2264 m	ν(Si-H)	878 m	ν(Si-F)
2182 s		849 m	
1050 m	ν(Si-N)(asym)	738 s	ρ(SiH_3 and/or SiH_2)
992 vs	δ(SiH_3 and/or SiH_2)	560 w	
950 vs		482 w	ν(Si-N)(sym)

[a] Tentative assignments of the major bands were made with the aid of detailed spectra reported for $(SiH_3)_3N$[7] and $(FSiMe_2)_2NH$.[15]

However, under the particular conditions chosen, we still observed the predominant formulation of $SiH_3N(SiH_2F)_2$ in the reaction. This differs from the results obtained in the chlorination of $(SiH_3)_3N$ using $SnCl_4$, where conditions could be chosen to favor the mono-, di-, or trichloro derivative. Variation of the reaction temperature was studied in our work. Temperatures below −50° seemed to prevent the reaction from occurring at all and we found that the optimum temperature range for fluorinating the silicon–hydrogen bond of the amine was between −23 and 0°, with the −23° temperature being recommended for synthetic work. At temperatures above 0°, the cleavage reaction was exclusive. Even at low temperatures, the cleavage reaction is very troublesome and the formation of SiH_2F_2 suggests that the silicon–nitrogen bonds of the fluorosilylamines themselves undergo cleavage.

Owing to its predominant formation in the reaction, the new compound $SiH_3N(SiH_2F)_2$ was the product most completely characterized in our study. The melting point of the material, determined by the Stock magnetic plunger method, is −89.7 ± 0.2°. Infrared absorption frequencies for $SiH_3N(SiH_2F)_2$ taken on a sample in the gas phase are given in Table I, with tentative assignments.

The proton NMR spectra of both $SiH_3N(SiH_2F)_2$ and $(FSiH_2)_3N$ were recorded. The SiH_2 protons of the latter compound appeared as a doublet ($J_{H-F} = 60.3$ Hz) centered at τ 5.15. The spectrum of $SiH_3N(SiH_2F_2)_2$ consisted of a doublet ($J_{H-F} = 60.3$ Hz) centered at τ 5.20 for the SiH_2 protons and a closely spaced triplet ($J_{H-F} = 1.5$ Hz) at τ 5.59 for the SiH_3 protons. The triplet arises from the long-range splitting of the SiH_3 protons by the two fluorines on the $FSiH_2$ groups. The peak areas were in the expected intensity ratios. The positions of the protons of the $FSiH_2$ groups are to the low field of $(SiH_3)_3N$ (τ 5.56)[16] as expected. The 60.3-Hz adjacent H–F coupling constants are consistent with the values for other systems with two electronegative atoms on silicon (e.g., J_{H-F} values for $FSiH_3$ and F_2SiH_2 are 45.8 and 60.5 Hz, respectively;[17] J_{H-F} of $(FSiH_2)_2O$ is 61.2 Hz).

It was somewhat puzzling to find that the silicon–hydrogen bonds of $[HSi(CH_3)_2Si]_2NH$ could not be fluorinated successfully with PF_5 without subsequent cleavage of the silicon–nitrogen bond. The presence of PF_3 and $(CH_3)_2SiF_2$ in the reaction products indicated that fluorination did occur; however, the only silicon products that we could detect were the fluoromethylsilanes $(CH_3)_2SiHF$ and $(CH_3)_2SiF_2$, at least under the conditions we chose to employ. The first step in the general silicon–nitrogen bond cleavage reaction most likely involves the coordination of the nitrogen of silazane to the phosphorus of the PF_5.[18] The increased basicity of the methylated amine would tend to promote this step and hence favor the cleavage. Only when the basicity of the silylamine is low as in the case of $(SiH_3)_3N$ can the hydrogen–fluorine exchange proceed satisfactorily without subsequent cleavage of the silicon–nitrogen bond. We did not pursue the fluorination of $[H(CH_3)_2Si]_2NH$ any further since $[F(CH_3)_2Si]_2NH$ has previously been prepared by the reaction of $[(CH_3)_2SiNH]_4$ with $F_4Si(NH_3)_2$.[15] The lesson to be learned from this result is that in the general fluorination of the silicon–hydrogen bond of hydrosilyl derivatives by PF_5, small differences in molecular composition may cause the undesired cleavage reaction to be favored exclusively.

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Registry No. $(FSiH_2)_2NSiH_3$, 56689-17-9; $(SiH_3)_3N$, 13862-16-3; PF_5, 7647-19-0; $(FSiH_2)_3N$, 56689-18-0.

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Electron Paramagnetic Resonance of Tris(ethyl xanthate)chromium(III)

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The spin-Hamiltonian parameters for d^3 complexes have been thoroughly elaborated within the context of molecular orbital theory[1-3] including charge-transfer effects, ligand spin–orbit effects,[1] and metal spin–orbit reduction.[2] From such theory, the molecular orbital mixing coefficients can, in principle, be determined if environmental effects are small.

Evaluation of lattice effects for a series of ionic complexes[3-5] indicates that spin-Hamiltonian parameters are intramolecular if host charge and site symmetry match those of the guest. Likewise, Kawasaki and Forster[6] have determined that lattice distortions for the ionic tris(oxalato)chromium(III) complex, a trigonal complex, cause a variation that can give a nonzero rhombic E parameter.

The effect of the lattice (environment) upon the spin-Hamiltonian parameters for molecular complexes has not been