Contribution from the Department of Chemistry, University of Colorado, Boulder, Colorado 80309,
and the Department of Chemistry, University of California, and the Materials and Molecular
Research Division of the Lawrence Berkeley Laboratory, Berkeley, California 94720

Reaction of Silylphosphine with Ammonia

ARLAN D. NORMAN* and WILLIAM L. JOLLY

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Silylphosphine (SiH_3PH_2) and NH_3 in the liquid phase react to form PH_3, $(SiH_3)_2NH$, and $(SiH_3)_3N$. No evidence for SiH_3NH_2 as an intermediate in the exchange processes could be obtained. Subsequent NH_3-promoted elimination of SiH_4 from silazane molecules yields a series of silazane oligomers and polymers. Two new condensation oligomers, $(SiH_3NH)_2SiH_2$ and $(SiH_3)_2NSiH_2N(H)SiH_3$, have been obtained in low yield. Chemical and spectral characterization data for the new silazanes are given. Possible mechanisms for the observed series of exchange and redistribution processes are discussed.

Introduction

The reaction of silylphosphine (SiH_3PH_2) with ammonia in the liquid phase was reported previously by Fritz and Berkenhoff to yield PH_3, SiH_4, and polymeric material of composition $[SiH_2(NH)]$.[1] They speculated that reaction occurs according to the sequence shown in eq 1a–c, although no direct evidence for the proposed intermediates or order of reactions was obtained.

$$SiH_3PH_2 + NH_3 \rightarrow SiH_3NH_2 + PH_3 \qquad (1a)$$

$$2SiH_3NH_2 \rightarrow (SiH_3)_2NH + NH_3 \qquad (1b)$$

$$(SiH_3)_2NH \rightarrow (1/n)[SiH_2(NH)]_n + SiH_4 \qquad (1c)$$

Since the early work of Fritz and Berkenhoff, several studies involving silylphosphines and silylamines (silazanes) have been reported which provide insight and some basis for understanding the SiH_3PH_2–NH_3 reaction system. Silyl-group exchange between SiH_3PH_2 and substituted amines has been demonstrated,[2] e.g., eq 2. Disilazane, $(SiH_3)_2NH$, has been

$$R_2NH + SiH_3PH_2 \rightarrow R_2NSiH_3 + PH_3 \qquad (2)$$
$$R = CH_3, C_2H_5$$

characterized and shown to undergo facile SiH_3-group redistribution[3,4] according to

$$3(SiH_3)_2NH \rightarrow 2(SiH_3)_3N + NH_3 \qquad (3)$$

The elimination of SiH_4 through hydrido (H) and amino (R_2N) group redistribution on silicon centers has been amply demonstrated,[2-11] and under carefully controlled conditions of base[8] (eq 4a) or acid[11] (eq 4b) catalysis, novel oligomeric condensation products have been obtained.

$$3(SiH_3)_3N \xrightarrow{\text{base}} (SiH_3NSiH_2)_3 + 3SiH_4 \qquad (4a)$$

$$2(SiH_3)_3N \xrightarrow{\text{acid}} (SiH_3)_2NSiH_2N(SiH_3)_2 + SiH_4 \qquad (4b)$$

The products of the SiH_3PH_2–NH_3 reaction reported previously are strongly indicative of the involvement of some combination of reactions of the types observed above. Therefore, in order to establish the detailed course of reaction and possibly to exploit the reaction as a source of new silazane compounds, we undertook a study of the system under carefully controlled conditions. Our results are described below.

Experimental Section

Apparatus and Materials. All manipulations were carried out in standard high-vacuum apparatus.[12] Mass spectra were obtained on Consolidated Electrodynamic Corp. (Model 620) and Varian MAT (CH-5 and CH-7) spectrometers. All data were obtained at an ionizing voltage of 70 eV. Infrared spectra were recorded with a Perkin-Elmer Model 337 spectrometer for gaseous samples in a 10-cm cell equipped with KBr windows. Proton NMR spectral data were obtained at 60.0 and 100.0 MHz on Varian A60-A and HA-100 spectrometers, respectively. Chemical shifts were measured relative to internal $(CH_3)_4Si$. Shifts downfield from the standard are recorded as positive ($+\delta$).

Silylphosphine was prepared by $LiAl(PH_2)_4$ phosphination of SiH_3Br[13] and ozonizer discharge reactions of SiH_4–PH_3 mixtures.[14] Ammonia (Matheson Co., anhydrous) dried at −78 °C over potassium and $(CH_3)_3N$ (Eastman Chemicals) dried over P_4O_{10} were low-temperature column distilled.[12]

General Procedures. Liquid-phase reactions of SiH_3PH_2 with NH_3 were carried out in heavy-wall NMR tubes or reaction bulbs equipped with Fischer-Porter O-ring valves. Gaseous-phase reactions were carried out in a double-bulb gas-mixing system equipped with Fischer-Porter needle valves. Reaction components were characterized by comparison of their physical and/or spectral properties with published values.

$SiH_3PH_2 + NH_3$. Silylphosphine (SiH_3PH_2) and NH_3 in reactant ratios ranging from 1.86 mmol:3.87 mmol (0.5:1.0) to 5.84 mmol:0.67 mmol (8.7:1.0) in 20–30-mL reaction bulbs were allowed to warm slowly to −78 °C. After reaction periods of 2–36 h at temperatures ranging from −78 to −45 °C, volatile reaction materials were removed and passed through traps at −78 and −135 °C into a −196 °C trap. No noncondensable gas was observed. After removal of high-volatility materials, the reaction vessel was warmed slowly to room temperature and the remaining materials were removed. Some reaction occurs during warming, as evidenced by effervescence of the reaction materials. The contents of the −78 and −135 °C traps were distilled repeatedly by using a low-temperature distillation column. The PH_3–SiH_4 mixture, condensed at −196 °C, was separated by complexation of the PH_3 with BCl_3 at −78 °C, at which temperature SiH_4 could be removed and measured. From a 21-h reaction of SiH_3PH_2 (2.26 mmol) with NH_3 (0.67 mmol), PH_3 (2.08 mmol), SiH_4 (0.45 mmol), unreacted NH_3 (0.17 mmol) and SiH_3PH_2 (0.24 mmol), $(SiH_3)_2NH$ (0.22 mmol), $(SiH_3)_3N$ (0.03 mmol), $(SiH_3NH)_2SiH_2$, I (0.005 mmol), $(SiH_3)_2NSiH_2N(H)SiH_3$, II (0.01 mmol), and $[(SiH_3)_2N]_2SiH_2$[11] (0.005 mmol) were typically obtained. In addition, small quantities of lower volatility material which could not be separated adequately but which exhibited mass spectral highest mass envelopes attributable to $Si_4N_3H_x^+$, $Si_5N_3H_x^+$, $Si_6N_3H_x^+$, and $Si_7N_3H_x^+$ were present. Substantial quantities of a nonvolatile, colorless residue remained in the reaction bulb. Yields of I, II, and $[(SiH_3)_2N]_2SiH_2$ were low, so fractions rich in them were accumulated from several reactions and the combined fraction was then column distilled.

Product yields varied considerably with the SiH_3PH_2:NH_3 reactant ratio. With low reactant ratios, somewhat higher yields of $(SiH_3)_2NH$ and II were obtained. However, because separation of reaction products from reactions in which large quantities of NH_3 was present was extremely difficult, these conditions were not pursued in detail.

Infrared and ^1H NMR spectral data for $(SiH_3NH)_2SiH_2$, I, and $(SiH_3)_2NSiH_2N(H)SiH_3$, II, are listed in Tables I and II. Infrared spectra of I and II are shown in Figure 1. Owing to the instability of I in the condensed phase, NMR spectra of sufficiently high quality to allow measurement of ^{29}Si satellite resonance data could not be obtained. The major peak of the parent and four most intense mass spectral envelopes of I occur at m/e (relative intensity) 120 (31), 88 (100), 72 (60), 43 (19), and 31 (10). The parent ion peak occurs at m/e 124. The major peak of the parent and four most intense mass spectral envelopes of II occur at m/e (relative intensity) 150 (28), 118 (100), 89 (19), 72 (67), and 31 (10). The parent ion peak occurs

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* To whom correspondence should be addressed at the University of Colorado.

Table I. Infrared Spectra of $(SiH_3NH)_2SiH_2$ (I) and $(SiH_3)_2NSiH_2N(H)SiH_3$ (II)[a]

I	II	tentative assignment[b,c]
3434 w	3436 w	ν(N–H)
2160 vs	2170 vs	ν(Si–H)
1185 s	1182 s	δ(N–H)
1102 m	1088 m	
	933 w, sh	
983 m, sh	975 w, sh	$\nu(Si–N–Si)_{asym}$
934 vs	944 vs	$\nu(SiH_3)$
839 s	893 vs	
833 w	834 w	
740 m	738 m	$\delta(SiH_3)_{rock}$

[a] All absorption maxima are in cm^{-1} units. Abbreviations: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder. [b] L. J. Bellamy, "The Infrared Spectra of Complex Molecules", 2nd ed., Wiley, New York, N.Y., 1958. [c] Reference 4.

Table II. Nuclear Magnetic Resonance Data[a]

	$(SiH_3NH)_2SiH_2$, I[b]	$(SiH'_3)_2NSiH_2$-$N(H)SiH_3$, II[c]
$\delta(SiH_3)$	4.35	4.37
$\delta(SiH_3')$		4.42
$\delta(SiH_2)$	4.62	4.63
$^3J(HNSiH_3)$	3.9 ± 0.3	3.8 ± 0.5[e]
$^3J(HNSiH_2)$	3.6 ± 0.3	4.0 ± 0.2
$^1J(^{29}SiH_3)$	*d*	210 ± 2
$^1J(^{29}SiH_3')$	*d*	212 ± 2
$^1J(^{29}SiH_2)$	*d*	224 ± 2

[a] Chemical shifts are given to ±0.02 ppm relative to $(CH_3)_4Si$. Coupling constants are in hertz. [b] Spectral data obtained on 5% by volume solutions in $(CH_3)_4Si$. [c] Spectral data obtained on 15–20% by volume solutions in $(CH_3)_4Si$. [d] Not measured; see text. [e] Large uncertainty in J arises from unresolved overlapped resonances.

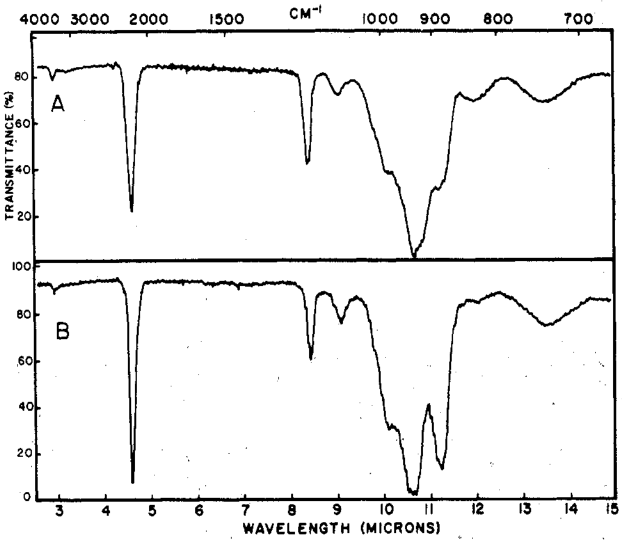

Figure 1. Infrared spectra of (A) $(SiH_3NH)_2SiH_2$, I, and (B) $(SiH_3)_2NSiH_2N(H)SiH_3$, II.

at m/e 152. A vapor density molecular weight of 151 (calcd 152.5) was obtained for II. I and II exhibit 0 °C vapor tensions of 10 and 4 torr, respectively. Their rapid thermal decomposition in the liquid phase precluded complete vapor tension vs. temperature measurements.

The decomposition of I and II for elemental analyses was accomplished by their cleavage with anhydrous HCl. The ratio of $HCl:SiH_3Cl:SiH_2Cl_2$ for I according to the equation $(SiH_3NH)_2SiH_2 + 6HCl \rightarrow 2NH_4Cl + SiH_2Cl_2 + 2SiH_3Cl$ is calculated as 6.00:1.00:2.00 and found to be 6.10:1.00:2.10. The ratio of $HCl:II:SiH_2Cl_2:SiH_3Cl$ for II according to the equation $(SiH_3)_2NSiH_2N(H)SiH_3 + 7HCl \rightarrow 2NH_4Cl + SiH_2Cl_2 + 3SiH_3Cl$ is calculated as 7.00:1.00:1.00:3.00 and found to be 7.10:1.00:1.05:3.08.

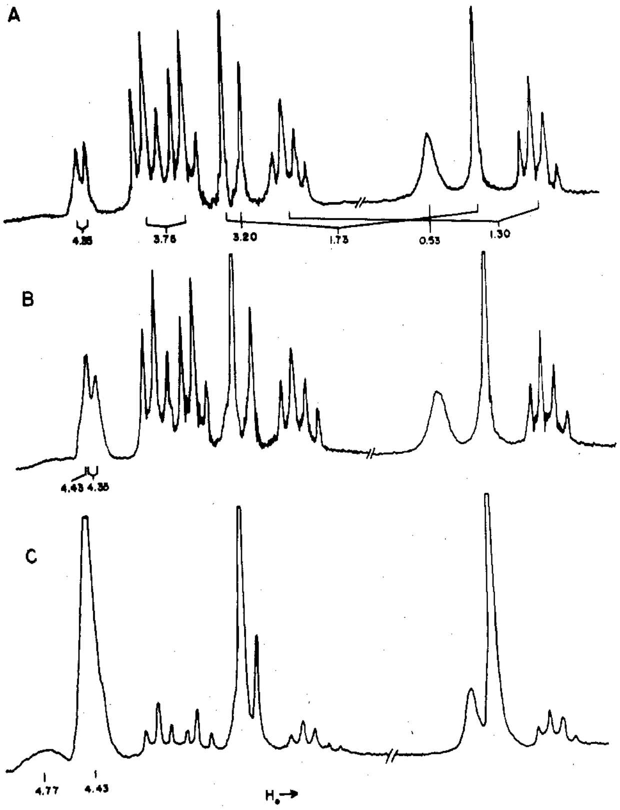

Figure 2. ^1H NMR spectra of the SiH_3PH_2–NH_3 reaction sequence: (A) after mixing at −70 °C, (B) after 40 min at −70 °C, and (C) after 60 min at 25 °C.

The low-volatility and nonvolatile residues from the SiH_3PH_2–NH_3 reaction were allowed to react with excess HCl. Immediate reaction occurs, with the formation of NH_4Cl and the evolution of SiH_3Cl, SiH_2Cl_2, lesser quantities of $SiHCl_3$, and traces of PH_3. The low-volatility oils and nonvolatile residue yielded SiH_3Cl and SiH_2Cl_2 in molar ratios of approximately (1.5–2.1):1.0 and (0.4–0.8):1.0, respectively.

Silylphosphine and NH_3, contained initially in the gaseous phase in the separated bulbs of a gas-mixing apparatus at pressures ranging from 0.25 to 0.8 torr, were allowed to mix. After being mixed, the reaction materials were sampled directly into the inlet of a mass spectrometer. Except for a trace of $(SiH_3)_2O$, due to reaction of spectrometer H_2O with SiH_3PH_2, no evidence of reaction was obtained. When the reactants were condensed at −78 °C briefly, flash evaporated into the vapor phase, and then sampled, only $(SiH_3)_2NH$, SiH_3PH_2, and NH_3 were evident.

SiH_3PH_2 and NH_3, contained in heavy-walled NMR tubes, were allowed to warm slowly to −78 °C while being shaken vigorously. Reactions were carried out neat or in $(CH_3)_4Si$ as solvent. Chemical shifts were measured relative to internal SiH_4 and secondarily referenced to $(CH_3)_4Si$. Initial ^1H NMR spectra were obtained at −70 to −75 °C, and subsequent spectra were obtained as a function of time at temperatures up to ambient probe temperature. A typical reaction sequence using SiH_3PH_2 (0.86 mmol) and NH_3 (0.41 mmol) is shown in Figure 2. Reaction quantities were determined by machine integration or, in regions of closely overlapped peaks, by manual measurement of peak heights.

SiH_3PH_2 + $(CH_3)_3N$. SiH_3PH_2 (1.0 mmol) and $(CH_3)_3N$ (0.60 mmol) in an NMR tube were allowed to stand at 25 °C. The ^1H NMR spectrum was measured daily for 14 days, after which the solution remained colorless. Resonances attributable to small quantities of $(SiH_3)_2PH$, $(SiH_3)_3P$, and PH_3 and a trace of SiH_4 were evident in the spectra. On the basis of spectral integration, it was estimated that less than 5% of the SiH_3PH_2 had reacted.

SiH_3PH_2 + $(SiH_3)_2NH$. $(SiH_3)_2NH$ (0.50 mmol) and SiH_3PH_2 (0.78 mmol) were dissolved in 8.0 mmol of $(CH_3)_4Si$ in an NMR tube. The sample was warmed to probe temperature (38 °C) and spectra were obtained at 20-min intervals. After 60 min, no reaction was evident.

$(SiH_3)_3N + PH_3$. $(SiH_3)_3N$ (1.0 mmol) and PH_3 (1.0 mmol), dissolved in $(CH_3)_4Si$ in a heavy-walled NMR tube, were warmed to room temperature. Resonances due to only $(SiH_3)_3N$ and PH_3 were evident. Examination of the spectrum baseline at high spectral amplitudes after 2 h at 38 °C revealed no resonances due to reaction products.

Results and Discussion

Exchange and Condensation Reactions. Silylphosphine and NH_3 undergo a sequence of reactions in the liquid phase to produce a complex product mixture whose composition is a function of reaction time, reaction temperature, and reactant ratio. Under carefully controlled conditions, product separation can be achieved. From this information the general sequence of reactions which occurs in the SiH_3PH_2–NH_3 system can be determined. In addition the reaction system provides a source of previously uncharacterized oligomeric silazane species $(SiH_3NH)_2SiH_2$ (I) and $(SiH_3)_2NSiH_2N(H)SiH_3$ (II).

The reaction of SiH_3PH_2 with NH_3 at −78 to −63 °C, in reactions where the $SiH_3PH_2{:}NH_3$ mole ratio is higher than ca. 6:1, results in the formation of mainly PH_3 and $(SiH_3)_2NH$ in a near 2:1 ratio. After 3 h, the reaction appears complete and only traces of NH_3 remain. Small quantities of $(SiH_3)_3N$ and SiH_4, the result of subsequent reactions, are evident also. The stoichiometry of the principal reaction appears to be

$$2SiH_3PH_2 + NH_3 \rightarrow (SiH_3)_2NH + 2PH_3 \qquad (5)$$

If the SiH_3PH_2–NH_3 reaction is allowed to proceed for longer periods of time, at temperatures above −78 °C or under conditions of lower $SiH_3PH_2{:}NH_3$ reactant ratios, further reaction leading to a complex mixture of products occurs. In addition to $(SiH_3)_2NH$ and PH_3, reaction mixtures contain substantial SiH_4 and $(SiH_3)_3N$, unreacted NH_3 and SiH_3PH_2, the new silazane oligomers $(SiH_3NH)_2SiH_2$ (I) and $(SiH_3)_2NSiH_2N(H)SiH_3$ (II), $[(SiH_3)_2N]_2SiH_2$, and a series of only partially characterized high molecular weight silazane oligomers. The characterization of I and II is described below.

A detailed understanding of the exchange and redistribution reactions which lead to the observed products is obtained by monitoring the ^1H NMR spectra of SiH_3PH_2–NH_3 reaction mixtures as a function of reaction time. A typical experiment, using a 2.0:1.0 $SiH_3PH_2{:}NH_3$ reactant ratio, is shown in Figure 2A–C. At −70 °C, immediately after reagent mixing (Figure 2A), resonances due to SiH_3PH_2 (δ 3.75 and 1.30[15]), NH_3 (δ 0.53[16]), small quantities of $(SiH_3)_2NH$ (δ 4.35[17]), SiH_4 (δ 3.20[18]), and PH_3 (δ 1.73[19]) are seen. After 40 min at 70 °C (Figure 2B), the PH_3 and $(SiH_3)_2NH$ and to a lesser extent SiH_4 resonances have increased markedly. Since PH_3 and SiH_4 are highly volatile and were largely in the vapor phase, no attempt was made to measure their rates of appearance or relative intensities quantitatively. The asymmetry on the low-field line of the $(SiH_3)_2NH$ doublet resonance is due to the appearance of the $(SiH_3)_3N$ resonance (δ 4.43[20]). With longer reaction times and/or upon warming of the sample, SiH_3PH_2 and NH_3 continually decrease, PH_3 and SiH_4 increase, and the resonances characteristic of $(SiH_3)_2NH$, $(SiH_3)_3N$, and silazane oligomers increase in intensity. After 1 h at room temperature (Figure 2C), broad unresolved resonances at δ 4.77 and 4.43 are clearly evident and continue to grow as reaction proceeds.

Comparison of the resonances at δ 4.77 and 4.43 with data available previously for $(SiH_3)_3N$, $(SiH_3)_2NH$, the silazane oligomers $[(SiH_3)_2N]_2SiH_2$ and $(CH_3NSiH_3)_2SiH_2$,[11] and the new oligomers I and II allows their unambiguous assignment to protons on silicon in environments $>NSiH_2N<$ and $>NSiH_3$, respectively. In the experiment shown in Figure 2A–C, the $SiH_3{:}SiH_2$ group molar ratio reached a value of ca. 3:1 after 4 h at room temperature. At that time, the reaction solution had become too viscous to allow further spectral analysis.

The spectral data obtained support the conclusion that the first products of the SiH_3PH_2–NH_3 reaction are $(SiH_3)_2NH$ and PH_3 as described in eq 5, in what is a SiH_3-group exchange reaction. It seems likely that SiH_3NH_2 is formed in an exchange prior to $(SiH_3)_2NH$, i.e.

$$SiH_3PH_2 + NH_3 \rightarrow SiH_3NH_2 + PH_3 \qquad (6)$$

however, this elusive species has not been observed previously.[4,5] Several experiments were done to check explicitly for its existence. SiH_3PH_2 with a great deficiency of NH_3 in $(CH_3)_4Si$ solvent was allowed to warm slowly in the NMR spectrometer from −90 °C with continual spectral monitoring on the chance that resonances in the silazane region other than $(SiH_3)_2NH$ or $(SiH_3)_3N$ might appear. The first peaks observed could be attributed to $(SiH_3)_2NH$. Finally, reactions of SiH_3PH_2 with NH_3 in the gas phase, in an apparatus arranged so that the gas mixture could be sampled directly into a mass spectrometer, were carried out. There was no evidence for reaction. After the reactants were condensed, only ion fragments due to $(SiH_3)_2NH$, SiH_3PH_2, NH_3, and small quantities of $(SiH_3)_3N$ were seen.

The sequence of reactions which leads to $(SiH_3)_2NH$ and $(SiH_3)_3N$ remains somewhat unclear. $(SiH_3)_2NH$ may form via redistribution of SiH_3NH_2 as

$$2SiH_3NH_2 \rightarrow (SiH_3)_2NH + NH_3 \qquad (7)$$

or through exchange of SiH_3NH_2 with SiH_3PH_2 as

$$SiH_3PH_2 + SiH_3NH_2 \rightarrow (SiH_3)_2NH + PH_3 \qquad (8)$$

The $(SiH_3)_3N$ formation, subsequent to that of $(SiH_3)_2NH$, appears not to be the result of the spontaneous redistribution of $(SiH_3)_2NH$ described earlier[4] (eq 9) since in NMR ex-

$$3(SiH_3)_2NH \rightarrow 2(SiH_3)_3N + NH_3 \qquad (9)$$

periments with $(SiH_3)_2NH$ in $(CH_3)_4Si$ solvent no measurable reaction was evident after periods of 30 min. Neither is it the result of $(SiH_3)_2NH$ exchange with SiH_3PH_2 since in NMR tube reactions they show no evidence of reaction. The dominant process may involve the reaction

$$(SiH_3)_2NH + SiH_3NH_2 \rightarrow (SiH_3)_3N + NH_3 \qquad (10)$$

a process in which SiH_3NH_2 (formed in eq 6) reacts directly with $(SiH_3)_2NH$ but at a rate somewhat slower than the process given in eq 5.

The formation of SiH_4 and silazane oligomers and polymers in the SiH_3PH_2–NH_3 reaction system can be accounted for by a series of NH_3-promoted condensation reactions involving $(SiH_3)_2NH$ and $(SiH_3)_3N$ and subsequent generations of silazane oligomers. The observed processes are examples of the well-established reactions where SiH_4 forms as a result of silyl (SiH_3) and amino (R_2N) group redistribution on a silicon center.[2-11] No evidence for oligomerization of silylphosphines, i.e.

$$2SiH_3PH_2 \rightarrow H_2PSiH_2PH_2 + SiH_4 \qquad (11)$$

or the formation of mixed silylphosphine–silylamine oligomers or polymers was obtained. Condensation, with SiH_4 elimination, can occur between two $(SiH_3)_2NH$ molecules to yield a first generation of oligomers $(SiH_3NH)_2SiH_2$, $(SiH_3)_2NSiH_2N(H)SiH_3$, and $[(SiH_3)_2N]_2SiH_2$, as shown in Figure 3. Interconversion among these can undoubtedly occur also, as a result of SiH_3-group exchange reactions. Further reaction of these oligomers with $(SiH_3)_2NH$, $(SiH_3)_3N$, and each other would lead ultimately to the higher molecular weight of $Si_4N_3H_x$, $Si_5N_3H_x$, $Si_6N_3H_x$, $Si_7N_3H_x$, etc. silazane oils and silazane polymers.

Wells and Schaeffer obtained $(SiH_3NSiH_2)_3$ from the base-promoted disproportionation of $(SiH_3)_3N$.[8] Aylett and Hakim reported tentatively the presence of a compound

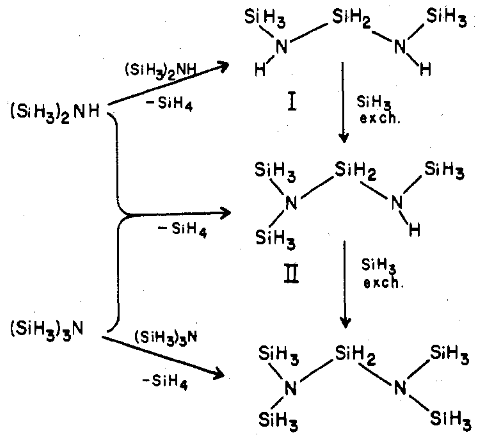

Figure 3. Proposed silazane redistribution scheme.

$(SiH_3NH)_2SiH_2$ as a byproduct of $(SiH_3)_2NH$ formation reactions.[4] The latter product seems likely to be the same as our compound I. Since $(SiH_3)_3N$ is a minor product in the SiH_3PH_2–NH_3 reaction system, $(SiH_3NSiH_2)_3$ would be expected to be present in very low yield. It may be a component of the uncharacterized low-volatility reaction products, although we did not explicitly identify it.

In summary, it appears that the SiH_3PH_2–NH_3 reaction proceeds through a sequence of reactions involving (i) initial SiH_3PH_2–NH_3 exchange, (ii) formation of $(SiH_3)_2NH$ and $(SiH_3)_3N$ through secondary redistribution reactions, and finally (iii) a series of SiH_4 elimination reactions to yield silazane oligomers and polymers. It seems likely that if reactions of SiH_3PH_2 and primary and secondary amines are examined in detail, similar sequences of reactions can be identified and additional new silazane oligomers can be isolated.

Characterization of $(SiH_3NH)_2SiH_2$ (I) and $(SiH_3)_2NSiH_2N(H)SiH_3$ (II). Characterization of I and II is based on elemental analyses, vapor density molecular weight (for II) and infrared, ^1H NMR, and mass spectral data. The mass spectra of I and II exhibit the expected silazane fragmentation patterns. In the polyisotopic spectra, the parent ion peaks at m/e 124 and 152 are readily assigned to the ion species $^{28}Si_3N_2H_{10}^+$ and $^{28}Si_4N_2H_{12}^+$, respectively. Species containing more than one of the less abundant ^{29}Si and ^{30}Si isotopes would not be intense enough to be seen. However, in both cases, small peaks, above the parent assignable to ^{29}Si and ^{30}Si isotope species, are evident.

Infrared spectral data for I and II, along with tentative peak assignments arrived at by comparisons of data and assignments made for other silazanes, are given in Table I. Absorptions at 3434 cm^{-1} (I) and 3436 cm^{-1} (II) characteristic of N–H stretching vibrations are especially important to note, since a N–H resonance cannot be seen in the ^1H NMR spectra of either I or II.

The ^1H NMR spectra of I and II show generally the features characteristic of silazanes. Spectral data and assignments are given in Table II. As has been the case with other NH-containing silazanes, a resonance due to the NH protons is not evident.[20–23] Attempts to locate the resonance through $^1H\{^{14}N\}$ decoupling were unsuccessful. Only with ^{15}N labeling could the NH resonance of $[(CH_3)_3Si]_2NH$ be identified.[20] Assignment of the δ 4.35 resonance in I and the δ 4.37 and 4.42 resonances in II to terminal SiH_3 groups on nitrogen agrees closely with the SiH_3 resonance positions of δ 4.44 $[(SiH_3)_3N]$, δ 4.34 $[(SiH_3)_2NH]$, and δ 4.43 $\{[(SiH_3)_2N]_2SiH_2\}$ reported earlier. Similarly, the SiH_2 resonances at δ 4.62 (I) and δ 4.63 (II) agree closely with those reported at δ 4.75 and 4.55 for $[(SiH_3)_2N]_2SiH_2$ and $(SiH_3NCH_3)_2SiH_2$, respectively. Interestingly, although NH resonances for the compounds cannot be seen, ^3J(HNSiH) coupling constants of 3.6–3.9 Hz are clearly evident.

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Registry No. I, 27712-54-5; II, 68928-22-3; SiH_3PH_2, 14616-47-8; NH_3, 7664-41-7.

References and Notes

(1) (a) G. Fritz and H. O. Berkenhoff, *Z. Anorg. Allg. Chem.*, **289**, 250 (1957); (b) G. Fritz, *Angew. Chem.*, **78**, 80 (1960).
(2) C. Glidwell, *Inorg. Nucl. Chem. Lett.*, **10**, 39 (1974).
(3) B. J. Aylett and M. J. Hakim, *Inorg. Chem.*, **5**, 167 (1966).
(4) B. J. Aylett and M. J. Hakim, *J. Chem. Soc. A*, 639 (1969).
(5) A. Stock and C. Somieski, *Chem. Ber.*, **54**, 740 (1921).
(6) A. B. Burg, and E. S. Kulijan, *J. Am. Chem. Soc.*, **72**, 3103 (1950).
(7) B. J. Aylett and M. J. Hakim, *Chem. Ind. (London)*, 1626 (1965).
(8) R. L. Wells and R. Schaeffer, *J. Am. Chem. Soc.*, **88**, 37 (1966).
(9) B. J. Aylett and J. Emsley, *J. Chem. Soc. A*, 1918 (1967).
(10) B. J. Aylett and M. J. Hakim, *J. Chem. Soc. A*, 1788 (1969).
(11) W. M. Scantlin and A. D. Norman, *Inorg. Chem.*, **11**, 3082 (1972).
(12) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds", McGraw-Hill, New York, N.Y., 1969.
(13) A. D. Norman and D. C. Wingeleth, *Inorg. Chem.*, **9**, 98 (1970).
(14) S. D. Gokhale and W. L. Jolly, *Inorg. Chem.*, **3**, 1141 (1964).
(15) J. E. Drake and W. L. Jolly, *J. Chem. Phys.*, **38**, 1033 (1963).
(16) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy", Vol. 2, Pergamon Press, New York, N.Y., 1966.
(17) Although the $(SiH_3)_2NH$ preparation has been reported previously,[5] ^1H NMR spectral data have been measured for the first time in our work.
(18) E. A. V. Ebsworth, "Volatile Compounds of Silicon", Pergamon Press, New York, N.Y., 1963.
(19) E. A. V. Ebsworth and G. M. Sheldrick, *Trans. Faraday Soc.*, 1071 (1967).
(20) G. Rocktäschel, E. A. V. Ebsworth, D. W. H. Rankin, and J. C. Thompson, *Z. Naturforsch., B*, **23**, 598 (1968).
(21) R. P. Bush, N. C. Lloyd, and C. A. Pearce, *Chem. Commun.*, 1269 (1967).
(22) R. P. Bush and N. C. Lloyd, *J. Chem. Soc. A*, 257 (1969).