and is in agreement with the assignments in azomethane (1575 cm^{-1}),[28] *trans*-difluorodiazene (1522 cm^{-1}),[29] N_2H_2 (1552 cm^{-1}),[27] and N_2D_2 (1498 cm^{-1}).[27] We consistently found the N═N stretching band to be more intense in the N—D isomer of each pair of diazenes. Finally, each monosubstituted diazene has as its lowest frequency infrared band in the 400–4000-cm^{-1} region a type A band at 480–550 cm^{-1} which we assign to the C—N═N bend. Supporting this assignment are the C—N═N bend of azomethane at 596 cm^{-1} [28] and the C—C═C bend of propene at 417 cm^{-1}.[30]

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The Borane-Catalyzed Condensation of Trisilazane and *N*-Methyldisilazane[1]

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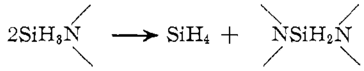
Diborane, B_5H_9, 1-BrB_5H_8, and 2-BrB_5H_8 catalyze the condensation of $(SiH_3)_3N$ and $CH_3N(SiH_3)_2$ in the liquid phase to yield silane and silazane oligomers and/or polymers. Under carefully controlled reaction conditions, the initial condensation oligomers, $[(SiH_3)_2N]_2SiH_2$ and $(SiH_3NCH_3)_2SiH_2$, can be obtained in good yields. Chemical and spectral characterization data for the new silazanes are given. A possible mechanism for the condensation is discussed.

Introduction

Silazane condensation reactions of the type



$$2SiH_3N\lt \longrightarrow SiH_4 + \gt NSiH_2N\lt \qquad (1)$$

are of interest for the synthesis of silicon–nitrogen bonds. Base-promoted reactions of this general type are well established.[2–5] Since silazanes are amphoteric, Lewis acid catalyzed reactions might also be expected if the acids are ones which do not readily cleave silicon–nitrogen bonds. Diborane might be expected to qualify as such an acid since it does not complex strongly enough with $(SiH_3)_3N$ or $CH_3N(SiH_3)_2$ to form an adduct or readily cleave the Si–N bonds. This is in contrast to the behavior of the stronger acid B_2H_5Br.[6] These considerations along with our interest in finding new routes to group IV–group V ternary hydrides has led us to examine reactions of $(SiH_3)_3N$ and $CH_3N(SiH_3)_2$ in the presence of B_2H_6, B_5H_9, 1-BrB_5H_8, and 2-BrB_5H_8. With these relatively weak acids, condensation does occur and we have succeeded in isolating and characterizing the initial condensation oligomers, $[(SiH_3)_2N]_2SiH_2$ and $(SiH_3NCH_3)_2SiH_2$.

Experimental Section

Apparatus.—All work was carried out in a standard high-vacuum system.[7,8] Vapor pressure *vs.* temperature data were collected with an all-glass immersible tensimeter (mercury manometer). Melting points were obtained by the Stock magnetic plunger technique. Mass spectra were obtained on Varian MAT CH-5 and CH-7 spectrometers (ionizing voltage 70 eV). Infrared spectra were recorded with a Perkin-Elmer Model 337 spectrometer on gaseous samples in a 10-cm cell equipped with KBr windows. Proton nmr spectra were obtained at 60.0 and 100.0 MHz on Varian A-60A and HA-100 spectrometers, respectively. Proton chemical shifts are reported relative to internal $(CH_3)_4Si$. Boron-11 nmr data were obtained with a Varian HA-100 equipped with standard 32.1-MHz probe and rf unit accessories.

Materials.—Diborane,[9] 1-BrB_5H_8,[10] 2-BrB_5H_8,[11] and $(SiH_3)_3N$[12] were prepared and purified using standard methods. The $CH_3N(SiH_3)_2$[13] was prepared using a reaction analogous to that described for $(SiH_3)_3N$. Pentaborane(9) (Callery Chemical Co.), HBr, and HCl (Matheson) were purified by routine fractional condensation techniques. In every case, compound purity was established by comparison of infrared, nmr, and physical property data with previously published values.

Borane-Catalyzed Condensations.—Typical borane-catalyzed condensation reactions of $(SiH_3)_3N$ and $CH_3N(SiH_3)_2$ are shown in Table I. In each case the reactants were condensed into 5–10-ml reaction tubes and allowed to warm to the indicated reaction temperature. In all experiments shown in Table I a liquid phase was present during the reaction. After the specified time, reaction materials were removed to the vacuum line, separated by routine fractional condensation, and characterized as outlined below. No hydrogen was formed in any of the reactions. Known components were characterized by comparison of their physical and/or spectral properties with literature values (confirmation methods in parentheses): SiH_4 (ir spectrum[14]), B_2H_6 (ir spectrum[15] and −112° vapor tension[16]), B_5H_9 (ir[17] and ^{11}B nmr[18] spectra), 1-BrB_5H_8 (^{11}B nmr spectrum[18]), 2-BrB_5H_8 (^{11}B

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[1] (a) Supported by National Science Foundation Grant GP-23575. (b) Based in part on M.S. Thesis of William M. Scantlin, Sept 1971, University of Colorado.

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TABLE I

TYPICAL SILAZANE CONDENSATION REACTIONS

Expt. No.	Reactants (mmol)	Time[a] (temp, °C)	Recovered materials (mmol)
1	$(SiH_3)_3N$ (2.50) B_5H_9 (0.10)	5.0 days (45)	SiH_4 (0.38) $(SiH_3)_3N$ (1.71)[b] B_5H_9 (0.11) $[(SiH_3)_2N]_2SiH_2$ (0.36) $Si_7N_3H_{16}$ (trace)[c]
2	$(SiH_3)_3N$ (1.35)	5.0 days (45)	$(SiH_3)_3N$ (1.33) No detectable products[d]
3	$(SiH_3)_3N$ (0.09) B_5H_9 (1.02)	8.5 days (25)	SiH_4 (0.10) B_5H_9 (1.04) $[(SiH_3)_2N]_2SiH_2$ (trace) High molecular weight materials: $Si_7N_3H_{16}$[c] and involatile solid
4	$(SiH_3)_3N$ (1.81) B_2H_6 (0.05)	4.0 days (25)	SiH_4 (0.52) B_2H_6 (0.04)[e] $(SiH_3)_3N$ (0.89) $[(SiH_3)_2N]_2SiH_2$ (0.4) $Si_7N_3H_{16}$ (trace)[c]
5	$(SiH_3)_3N$ (0.32) 1-BrB_5H_8 (0.05)	3.5 hr (25)	SiH_4 (0.08) $(SiH_3)_3N$ (0.18) 1-BrB_5H_8[f] $[(SiH_3)_2N]_2SiH_2$[f] Involatile solid
6	$(SiH_3)_3N$ (0.55) 2-BrB_5H_8 (0.08)	3.5 hr (25)	SiH_4 (0.33) $(SiH_3)_3N$ (0.13) 2-BrB_5H_8[f] $[(SiH_3)_2N]_2SiH_2$[f] Involatile solid
7	$CH_3N(SiH_3)_2$ (1.20) B_5H_9 (0.05)	14 hr (25)	SiH_4 (0.34) $CH_3N(SiH_3)_2$ (0.53)[b] B_5H_9 (0.05) $(SiH_3NCH_3)_2SiH_2$ (0.30) Trace of low volatility liquids

[a] Reaction temperatures are given to ±2° and times to ±0.5 hr. [b] Separated quantitatively from B_5H_9 by conversion to NRH_3Br ($R = H$ or CH_3) and SiH_3Br by reaction with excess HBr. [c] Characterized from mass spectral data only. [d] Within experimental error, the $(SiH_3)_3N$ was recovered quantitatively. [e] Separated from the SiH_4 by complexation with $(CH_3)_3N$. [f] Not separated. Components characterized by ^{11}B and ^1H nmr spectral data.

nmr spectrum[18]), $(SiH_3)_3N$ (ir spectrum[19] and 0° vapor tension[20]), $CH_3N(SiH_3)_2$ (0° vapor tension).[21] Analytically pure samples of $[(SiH_3)_2N)]_2SiH_2$ and $(SiH_3NCH_3)_2SiH_2$ were obtained by their repeated passage through traps at −15 and −30°, respectively, into a −63° trap.

Elemental Analyses.—The decomposition of $[(SiH_3)_2N]_2SiH_2$ and $(SiH_3NCH_3)_2SiH_2$ for elemental analyses was accomplished by reactions of weighed samples with anhydrous HBr. The ratio of $HBr:NH_4Br:SiH_3Br:SiH_2Br_2$ for $[(SiH_3)_2N]_2SiH_2$ according to the equation

$$[(SiH_3)_2N]_2SiH_2 + 8HBr \longrightarrow 2NH_4Br + 4SiH_3Br + SiH_2Br_2$$

is calcd, 8.00:2.00:4.00:1.00; found, 8.12:2.05:4.00:0.95. The ratio of $HBr:CH_3NH_3Br:SiH_3Br:SiH_2Br_2$ for $(SiH_3NCH_3)_2SiH_2$ according to the equation

$$(SiH_3NCH_3)_2SiH_2 + 6HBr \longrightarrow 2CH_3NH_3Br + 2SiH_3Br + SiH_2Br_2$$

is calcd, 6.00:2.00:2.00:1.00; found, 6.07:2.12:1.92:1.03.

Vapor Pressure *vs.* Temperature Data. (A) $[(SiH_3)N]_2SiH_2$.—Vapor pressures in the range 0.0–51.0° are given in Table II and are represented by the equation

$$\log P_{mm} = \frac{-2.083 \times 10^3}{T} + 8.042$$

TABLE II

VAPOR PRESSURE *vs.* TEMPERATURE DATA

$[(SiH_3)_2N]_2SiH_2$[a]			$(SiH_3NCH_3)_2SiH_2$[b]		
Temp, °C	P_{mm}		Temp, °C	P_{mm}	
	Obsd	Calcd		Obsd	Calcd
0.0	2.5	2.1	0.0	5.0	5.0
10.4	4.4	4.9	8.8	8.9	8.8
18.5	8.8	7.9	15.4	13.4	13.2
27.5	13.2	13.0	20.5	17.7	17.9
32.8	17.0	17.0	28.0	27.0	27.2
39.7	23.7	24.2	36.0	42.5	41.6
44.0	30.2	29.7	44.0	62.5	61.6
51.0	40.5	41.2	0.0[c]	7.0	5.0
0.0[c]	3.2	2.1			

[a] Measurement over a 2.5 hr period. [b] Measurement over a 1.5 hr period. [c] Pressure observed on decreasing the temperature.

Slight sample decomposition occurred as evidenced by the increase in the 0° vapor tension at the end of the analysis. The extrapolated boiling point is 131°, the molar heat of vaporization is 9.50 kcal mol^{-1}, and Trouton's constant is 23.6 cal deg^{-1} mol^{-1}.

(B) $(SiH_3NCH_3)_2SiH_2$.—Vapor pressures were measured over the range 0.0–44.0°. Pressures at temperatures greater than 44° could not be obtained since sample decomposition was evident. Vapor pressures are represented by the equation

$$\log P_{mm} = \frac{-2.157 \times 10^3}{T} + 8.597$$

The extrapolated boiling point is 103°, the molar heat of vaporization is 9.94 kcal, and Trouton's constant is 26.3 cal deg^{-1} mol^{-1}.

Spectral Data. (A) $[(SiH_3)_2N]_2SiH_2$.—Infrared absorptions occur at λ_{max} 2172 (vs), 1025 (m, sh), 1000 (s, sh), 980 (s, sh), 952 (vs), 877 (vs), 769 (w, sh), and 741 (m) cm^{-1}. The mass spectrum exhibits a highest mass peak at *m/e* 185 (relative intensity 0.4% of the most intense peak at *m/e* 149). Proton nuclear magnetic resonance data are listed in Table III.

TABLE III

NUCLEAR MAGNETIC RESONANCE DATA[a]

	$[(SiH_3)_2N]_2SiH_2$[b]	$(SiH_3NCH_3)_2SiH_2$[b]
$\delta(SiH_3)$	−4.43 (12)	−4.38 (6)
$\delta(SiH_2)$	−4.75 (2)	−4.55 (2)
$\delta(CH_3)$		−2.58 (6)
$^1J(^{29}SiH_3)$	213 ± 1	209 ± 1
$^1J(^{29}SiH_2)$	228 ± 2	224 ± 2

[a] Chemical shifts are given to ±0.02 ppm relative to $(CH_3)_4Si$; a minus δ value is downfield from $(CH_3)_4Si$. [b] Relative peak areas are given in parentheses.

(B) $(SiH_3NCH_3)_2SiH_2$.—Infrared absorptions occur at λ_{max} 2932 (m), 2898 (m), 2816 (m), 2183 (s), 2136 (vs), 1519 (w), 1481 (w), 1197 (s), 1093 (vs), 991 (m, sh), 931 (vs), 893 (vs), 855 (w, sh), and 714 (s) cm^{-1}. The mass spectrum exhibits a highest mass peak at *m/e* 153 (relative intensity 0.9% of the most intense peak at *m/e* 119). Proton nuclear magnetic resonance data are shown in Table III.

Results and Discussion

Condensation Reactions.—The borane-catalyzed silazane condensation reactions were studied under conditions shown in Table I. Reactions were studied at 25 and 45°, as a function of time, and at varying borane:reactant silazane ratios. In all reactions, a liquid phase was present. Four boranes, B_2H_6, B_5H_9, 1-BrB_5H_8, and 2-BrB_5H_8, were examined as catalysts. In all of the systems studied, condensation occurs with the elimination of SiH_4 and the formation of new silazane oligomeric and/or polymer products.

Pentaborane and B_2H_6-catalyzed reactions occur more slowly than those with 1- or 2-BrB_5H_8, and at a controllable rate such that the products obtained are

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primarily those of the first condensation step (expt 1, 4, and 7).

$$2(\mathrm{SiH_3})_2\mathrm{NR} \longrightarrow \mathrm{SiH_4} + (\mathrm{SiH_3NR})_2\mathrm{SiH_2} \qquad (2)$$
$$(\mathrm{R} = \mathrm{CH_3} \text{ or } \mathrm{SiH_3})$$

The borane catalysts were recovered quantitatively in these reactions within experimental error and no evidence for boron-containing products was obtained. Traces of higher molecular weight silazane material of composition $\mathrm{Si_7N_3H_{16}}$ and $\mathrm{C_2Si_3N_3H_{16}}$, from $(\mathrm{SiH_3})_3\mathrm{N}$ and $\mathrm{CH_3N(SiH_3)_2}$ reactions, respectively, are formed and were characterized tentatively by mass spectral analyses. In addition, traces of involatile oil, presumed to be silazane polymer, remain in the reaction vessels. The presence of higher molecular weight silazanes indicates that even under carefully controlled conditions, a small amount of condensation beyond the first step occurs.

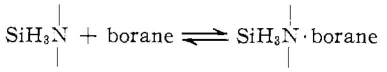
Reactions catalyzed by 1-$\mathrm{BrB_5H_8}$ or 2-$\mathrm{BrB_5H_8}$ (expt 5 and 6) or $\mathrm{B_2H_6}$ or $\mathrm{B_5H_9}$ where the borane:reactant silazane ratio is high (expt 3) proceed considerably beyond the first condensation step as is shown by the $\mathrm{SiH_4}$:$(\mathrm{SiH_3NR})_2\mathrm{SiH_2}$ product ratio being in excess of 1:1 and by the formation of considerable amounts of high molecular weight oligomeric and polymeric products. From reactions in which the reactant silazane was consumed completely (expt 3), it appears that a final reactant silazane:product $\mathrm{SiH_4}$ ratio of 1:1 is approached and that the overall condensation can be written as

$$n(\mathrm{SiH_3})_2\mathrm{NR} \longrightarrow (\mathrm{SiH_2NR})_n + n\mathrm{SiH_4} \qquad (3)$$

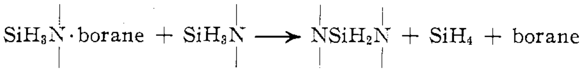
The catalytic role of the boranes in these liquid-phase condensation reactions appears well established on the bases that no detectable condensation in the absence of the boranes occurs (expt 1 and 2) and complete recovery of $\mathrm{B_5H_9}$ and $\mathrm{B_2H_6}$ in expt 1, 4, and 7 was accomplished. No evidence for boron-containing products was obtained.

No boron-containing products were observed also in the 1-$\mathrm{BrB_5H_8}$ and 2-$\mathrm{BrB_5H_8}$ reactions. However, we did not attempt to recover quantitatively the boranes from these reaction mixtures. Therefore, it is possible that some reaction of these catalysts with the silazane substrate occurs. Based on the earlier studies by Burg on reactions of diboranes with silazanes,[6] it might be expected that cleavage of SiN bonds by boron–bromine bonds would occur. Similar cleavage processes occurring concurrent with the catalyzed condensations seem likely for the bromopentaboranes; however, they were not detected.

The mechanism by which the acid-catalyzed condensation occurs requires further investigation. However, sufficient data have been obtained to allow tentative conclusions to be made. Our results suggest that the order of effectiveness of the boranes as catalysts is $\mathrm{B_5H_9} < \mathrm{B_2H_6} <$ 1-$\mathrm{Br_5H_8} \simeq$ 2-$\mathrm{BrB_5H_8}$, paralleling their presumed Lewis acid strength toward silazanes. Reaction rates are enhanced by increasing the borane:silazane ratio (expt 1 and 4) and under comparable reaction conditions, $\mathrm{CH_3N(SiH_3)_2}$ undergoes condensation more rapidly than $(\mathrm{SiH_3})_3\mathrm{N}$ (expt 1 and 7). These data suggest the importance of silazane–borane complexation in the initial reaction steps and are consistent with a series of steps as shown in eq 4a and 4b. Continuation of these processes would result in the formation of higher order Si–N oligomers and polymers.

 (4a)

$$\mathrm{SiH_3\overset{|}{\underset{|}{N}} + borane \rightleftharpoons SiH_3\overset{|}{\underset{|}{N}}\cdot borane} \qquad (4a)$$

 (4b)

$$\mathrm{SiH_3\overset{|}{\underset{|}{N}}\cdot borane + SiH_3\overset{|}{\underset{|}{N}} \longrightarrow \overset{|}{\underset{|}{N}}SiH_2\overset{|}{\underset{|}{N}} + SiH_4 + borane} \qquad (4b)$$

Characterization of $[(\mathrm{SiH_3})_2\mathrm{N}]_2\mathrm{SiH_2}$ and $(\mathrm{SiH_3NCH_3})_2\mathrm{SiH_2}$.—Characterization of $[(\mathrm{SiH_3})_2\mathrm{N}]_2\mathrm{SiH_2}$ and $(\mathrm{SiH_3NCH_3})_2\mathrm{SiH_2}$ is established based on elemental analyses, vapor density molecular weights, and infrared, ^{1}H nmr, and mass spectral data. The $(\mathrm{SiH_3NCH_3})_2\mathrm{SiH_2}$ may have been observed previously by Aylett and Hakim in the base-promoted condensation of *N*-methyldisilazane;[4] however, unambiguous characterization data were not obtained by these authors.

The mass spectra of $[(\mathrm{SiH_3})_2\mathrm{N}]_2\mathrm{SiH_2}$ and $(\mathrm{SiH_3NCH_3})_2\mathrm{SiH_2}$ exhibit the expected silazane fragmentation patterns. In the polyisotopic spectra, the highest mass peaks at m/e 185 and m/e 153 can be attributed to the $^{28}\mathrm{Si_3}^{29}\mathrm{Si}^{30}\mathrm{SiN_2H_{14}}^+$ and $^{28}\mathrm{Si}^{29}\mathrm{Si}^{30}\mathrm{SiC_2N_2H_{14}}^+$ molecular ion species. Based on isotope abundance calculations for $\mathrm{Si_5}$ and $\mathrm{Si_3}$ clusters, it can be seen that the observation of ion species containing larger numbers of the lesser isotopes of silicon (*i.e.*, ^{29}Si and ^{30}Si) would not be expected under our experimental conditions.[22]

Comparison of the infrared spectral data with those published previously for other silazanes[23–27] allows assignment of several of the absorptions (assignments in parentheses): $(\mathrm{SiH_3NCH_3})_2\mathrm{SiH_2}$ 2932–2816 (CH str), 2183 (SiH str), 1197 ($\mathrm{CH_3}$ def), 933 ($\mathrm{SiH_3}$ def), and 714 cm^{-1} ($\mathrm{SiH_3}$ rock); $[(\mathrm{SiH_3})_2\mathrm{N}]_2\mathrm{SiH_2}$ 2172 (SiH str), 952 ($\mathrm{SiH_3}$ def), and 741 cm^{-1} ($\mathrm{SiH_3}$ rock).

The ^{1}H nmr spectra of $[(\mathrm{SiH_3})_2\mathrm{N}]_2\mathrm{SiH_2}$ and $(\mathrm{CH_3NSiH_3})_2\mathrm{N}$ show only featureless broad singlets, characteristic of silazanes. Silyl ($\mathrm{SiH_3}$) groups bonded to nitrogen typically lie in the range δ -4.60 to δ -4.10.[3] For $(\mathrm{SiH_3})_3\mathrm{N}$ and $(\mathrm{SiH_3})_2\mathrm{NCH_3}$ they occur at δ -4.44 ± 0.02.[28,29] The $\mathrm{CH_3}$ group resonances of $(\mathrm{SiH_3})_2\mathrm{NCH_3}$ occur at δ -2.55.[29] Based on comparison with the literature data and consideration of spectral peak area relationships, the assignment of spectral resonances shown in Table III is accomplished.

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