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Reactions of ((Organosilyl)amino)boranes with Selected Hydrides[1]

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When $(Me_3Si)_2NB(Cl)N(H)SiMe_3$ was allowed to react with $LiBH_4$, the isolated products were $(Me_3Si)_2NBH_2$, $[Me_3SiN(H)BH_2]_3$, and $[Me_3SiNBH]_3$. The reaction of $(Me_3Si)_2NB(H)N(H)SiMe_3$ with $THF\cdot BH_3$ gave $(Me_3Si)_2NBH_2$, $[Me_3SiN(H)BH_2]_3$, $[Me_3SiNBH]_3$, $(Me_3Si)_2HN_3B_3H_3$, and $(Me_3Si)_2NH$. On the other hand, $[Me_3SiN(H)BH_2]_3$, $[Me_3SiNBH]_3$, $(Me_3Si)_2HN_3B_3H_3$, and $(Me_3Si)H_2N_3B_3H_3$ were obtained from the reaction of $(Me_3Si)_2NB(Cl)N(H)SiMe_3$ with $THF\cdot BH_3$. The reaction of $(Me_3Si)_2NH$ and $THF\cdot BH_3$ produced $[Me_3SiN(H)BH_2]_3$, $(Me_3Si)_2NBH_2$, and *n*-$BuOB(H)N(SiMe_3)_2$ in low yields. From these results a reaction pathway is proposed and discussed for the reduction of $(Me_3Si)_2NB(Cl)N(H)SiMe_3$ with $LiBH_4$.

Introduction

In the area of boron–nitrogen chemistry, others have prepared (alkylamino)boranes by the reduction of (alkylamino)haloboranes using certain hydrides: for example, lithium tetrahydridoaluminate has been utilized to prepare bis(dimethylamino)borane[2] and bis(diethylamino)borane[3] from chlorobis(dimethylamino)borane and bis(diethylamino)fluoroborane, respectively. In addition, lithium hydride has been found to reduce both chlorobis(dimethylamino)borane and chlorobis(diethylamino)borane to the corresponding hydrides;[4] and dichloro(diethylamino)borane can be converted to (diethylamino)borane with sodium tetrahydroborate.[5] The latter hydride also was used to synthesize the 1,3,2-benzodiazaboroline from the corresponding B–Cl compound.[6]

As a part of our studies on silicon–nitrogen–boron compounds, it was of interest to determine if certain ((organosilyl)amino)boranes could be prepared by reduction of ((organosilyl)amino)haloboranes. During the investigation the isolation of unexpected products from the reaction of (bis(trimethylsilyl)amino)chloro((trimethylsilyl)amino)borane and lithium tetrahydroborate led to a further examination of this system. The results of this study and a proposed reaction pathway are presented.

Experimental Section

Materials and General Procedures. Lithium tetrahydroborate, lithium tetrahydridoaluminate, and borane in tetrahydrofuran (1 M) were purchased from Ventron Corp., Beverly, MA, and were used without repurification. Foote Mineral Co., Exton, PA, was the source for the 1.6 M solution of butyllithium in hexane. Hexamethyldisilazane was purchased from Dow Corning Corp., Midland, MI, and was redistilled prior to use. Tributyltin hydride was used without repurification and was acquired from K and K Laboratories, Inc., Plainview, NY. All solvents were dried over calcium hydride and distilled directly into the reaction flask. Trichloroborane was obtained as pressurized gas from the Matheson Co. and was used without further purification. The lithium bis(trimethylsilyl)amide was prepared by the method reported[7] and was distilled prior to use. (Bis(trimethylsilyl)amino)chloro((trimethylsilyl)amino)borane (I) was prepared by the procedure described by Wells and Collins.[8] (Bis(trimethylsilyl)amino)dichloroborane (VIII) was prepared by a method similar to that described in the literatue,[9,10] but lithium bis(trimethylsilyl)amide was used rather than the sodium salt.

All elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. A Picker-Nuclear Model MS-902 instrument was used to obtain high-resolution mass spectral data. Routine ^1H NMR spectra were obtained with Varian Model A60 and T60 spectrometers. The ^{11}B NMR spectra were recorded on a Varian Model HA 100 using a 32.1-MHz radio-frequency probe by Dr. Charles Moreland at North Carolina State University, Raleigh, NC. The IR spectral data were collected by means of a Perkin-Elmer Model 137 spectrophotometer. Gas chromatographic analyses and preparative scale separations were carried out with an Aerograph Autoprep Model A-700 gas chromatograph. The following two columns were purchased from Varian Aerograph, Walnut Creek, CA: column A, 30% SE-30 silicone gum rubber substrate on 45/60 mesh Chromosorb P (5 ft × $^{3}/_{8}$ in.); column B, 20% Apiezon L on 60/80 mesh firebrick (5 ft × 3/8 in.).

Reactions were conducted in 500- or 1000-mL round-bottom three-necked flasks to which a Friedrich condenser and rotatory stirrer were attached. The Friedrich condenser was connected to a vacuum manifold and an oil bubbler by means of a three-way stopcock. This enabled the reaction system to be evacuated to 0.05 torr and filled with dry nitrogen. During the reactions a steady stream of dry nitrogen was passed from the vacuum manifold through the oil bubbler. This allowed the reaction mixture to be under a nitrogen atmosphere at all times.

Boiling point, analytical, and molecular weight data are presented in Table I. Table II contains ^1H and ^{11}B NMR spectral data, and selected IR data are found in Table III.

Reaction of (Bis(trimethylsilyl)amino)chloro((trimethylsilyl)amino)borane (I) with Lithium Tetrahydroborate. To a stirred mixture of $LiBH_4$ (2.420 g, 111 mmol) in 500 mL of ether was added $(Me_3Si)_2NB(Cl)N(H)SiMe_3$ (31.85 g, 108 mmol). After the mixture had been heated to reflux for 2.5 h, a white solid was filtered from the reaction mixture under a dry-nitrogen atmosphere. The solvent was removed from the filtrate by vacuum distillation, and the remaining liquid was separated into several crude fractions via vacuum distillation.

While the first fwo fractions, bp 58–60 °C (89 torr) and 49 °C (50 torr), stood at room temperature for 2 weeks, $[Me_3SiN(H)BH_2]_3$ (IV) precipitated as a white solid (1.221 g, 11.3% yield based on I). From the third fraction $(Me_3Si)_2NBH_2$ (III) was distilled under vacuum as a clear colorless liquid (0.951 g, 5.1% yield based on I), and $[Me_3SiNBH]_3$ (V) was isolated by vacuum distillation from the last fraction (4.184 g, 39% yield based on I).

Synthesis of (Bis(trimethylsilyl)amino)((trimethylsilyl)amino)borane (II). To a stirred mixture of $LiAlH_4$ (3.028 g, 79.7 mmol) in 250 mL of ether was added I (19.23 g, 65.5 mmol). After the mixture had been heated to reflux for 39 h, a gray solid was filtered from the mixture and the solvent was removed from the filtrate by vacuum distillation. From the remaining residue $LiBH_4$ (0.052 g, 3.7% yield based on I) was filtered and identified from its IR spectrum. Vacuum

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[1] (a) Taken in part from: Nutt, W. R. Ph.D. Dissertation, Duke University, Durham, North Carolina, 1971. (b) Presented in part at the Southwest–Southeast Regional Meeting of the American Chemical Society, New Orleans, December 1970; see Abstracts, p 60.

[2] Coates, G. E. *J. Chem. Soc.* **1950**, 3481.

[3] Nöth, H.; Vahrenkamp, H. *Chem. Ber.* **1966**, *99*, 2757.

[4] Nöth, H.; Dorochov, W. A.; Fritz, P.; Pfab, F. *Z. Anorg. Allg. Chem.* **1962**, *318*, 293.

[5] Watanabe, H.; Nagasawa, K.; Totani, T.; Yoshizaki, T.; Nakagawa, T. "Boron-Nitrogen Chemistry"; American Chemical Society: Washington, D. C., 1964; Adv. Chem. Ser. No. 42, p 108.

[6] Hohnstedt, L. F.; Pellicciotto, A. M. *U.S. Dep. Commer., Off. Tech. Serv., PB Rep.* **1962**, *No. 152085*, 11; *Chem. Abstr.* **1963**, *58*, 2448c.

[7] "Inorganic Synthesis"; McGraw-Hill: New York, 1966; Vol. VIII, p 21.

[8] Wells, R. L.; Collins, A. L. *Inorg. Chem.* **1966**, *5*, 1327.

[9] Geymayer, P.; Rochow, E. G.; Wannagat, U. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 633.

[10] Geymayer, P.; Rochow, E. G. *Monatsh. Chem.* **1966**, *97*, 429.

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Table I. Boiling Point, Analytical, and Molecular Weight Data of Certain Silicon-Nitrogen-Boron Compounds

		calcd (found)					
compd	bp, °C (torr)	% C	% H	% B	% N	% Si	mol wt,[a] *m/e*
$(Me_3Si)_2NB(H)N(H)SiMe_3$ (II)	42 (0.55)	41.51 (41.43)	11.22 (10.81)	4.15 (4.01)	10.76 (11.06)	32.36 (32.00)	260.1732 (260.1718)
$(Me_3Si)_2NBH_2$ (III)	42–43 (15)	41.60 (41.40)	11.64 (11.72)	6.24 (6.24)	8.09 (7.62)	32.43 (31.47)	173.1227 (173.1226)
$[Me_3SiN(H)BH_2]_3$ (IV)[b]		35.66 (36.09)	11.97 (12.09)	10.71 (10.94)	13.86 (13.77)	27.80 (27.87)	303.2496 (303.2473)
$[Me_3SiNBH]_3$ (V)	71 (1.0)[c]	36.39 (36.32)	10.18 (10.40)	10.93 (10.92)	14.14 (14.13)	28.36 (28.07)	297.2027 (297.2012)
$(Me_3Si)_2HN_3B_3H_3$ (VI)	69 (5.5)	32.05 (32.28)	9.86 (10.13)	14.42 (14.76)	18.69 (18.48)	24.98 (24.75)	225.1632 (225.1632)

[a] The molecular ion was obtained from a high-resolution mass spectrum of the compound and the calculated value is based on the most abundant isotopes. [b] The elemental analysis was taken from Ph.D. dissertation of A. L. Collins[13]; mp 117 °C dec. [c] Literature bp 104 °C (0.95 torr).[14]

Table II. ^1H[a] and ^{11}B[b] Nuclear Magnetic Resonance Spectra of Certain Silicon-Nitrogen-Boron Compounds

compd	$\delta(Me_3Si)$	δ(BH)	δ(NH)	$\delta(^{11}B)$
$(Me_3Si)_2NB(H)N(H)SiMe_3$ (II)	−0.08 (s), −0.16 (s)	*c*	2.50[g] (s)	33.1 (s)
$(Me_3Si)_2NBH_2$ (III)	−0.10 (s)	*d*		47.8 (s)
$[Me_3SiN(H)BH_2]_3$ (IV)	−0.32 (s), −0.40 (s)	*c*	0.60[g] (s)	−10.6 (t)
$[Me_3SiNBH]_3$ (V)	−0.10 (s)	4.50[e] (s)		30.3 (s)
$(Me_3Si)_2HN_3B_3H_3$ (VI)	−0.12 (s)	*f*	5.16 (s)	32.3 (s)
n-$BuOB(H)N(SiMe_3)_2$ (IX)[i]	−0.06 (s)	*c*		33.7 (s)

[a] All spectra were obtained at ambient temperatures from neat-liquid samples except that of compound IV which was obtained from a saturated benzene or benzene-d_6 solution. All chemical shifts were determined with respect to Me_4Si by tube interchange. A negative value for the chemical shift indicates an upfield shift from Me_4Si: s = singlet, t = triplet, m = multiplet. [b] All spectra were obtained at ambient temperatures from neat-liquid samples except that of compound IV which was obtained from a saturated benzene or benzene-d_6 solution. Chemical shifts were determined with respect to $Et_2O{\cdot}BF_3$ by tube interchange, and a negative value for the chemical shift indicates an upfield shift from the reference. The symbol s is used for a broad (400–500 Hz) singlet. ^{11}B–H coupling was observed only for compound IV, and this triplet was unresolved. [c] No signal was observed at higher spectral amplitudes than those used to observe the C–H resonances. [d] While no signal was discernible at the spectral amplitudes which put the C–H resonance on scale, at higher amplitudes a broad band (200–300 Hz) was observed with its center at approximately δ 3.9 (Me_4Si). [e] No signal was distinguishable at the spectral amplitudes which put the C–H resonance on scale, but at higher amplitudes a broad singlet was obtained. The assignment of this band to the B–H resonance is in agreement with those made for the B–H resonances in borazine and *N*-methylborazines.[15–17] [f] At spectral amplitudes, which put the C–H resonance off scale, a broad band was found on the upfield side of the N–H resonance and was partially overlapped by the N–H resonance. It was not possible therefore to obtain a chemical shift. [g] At a spectral amplitude, which put the C–H resonances on scale, no signal was discernible, but at higher amplitudes a broad singlet was observed. [h] At spectral amplitudes, which put the C–H resonance off scale, a broad singlet was found. The assignment of this band to the N–H resonance is in agreement with those made for the N–H resonances in borazine and the *N*-methylborazines.[15–17] [i] Signals for the *n*-BuO group: δ 3.61 (t, CH_2O), 1.23 (m, CH_2CH_2), 0.69 (t, CH_3).

distillation afforded II (1.411 g, 8.3% yield).

Reaction of (Bis(trimethylsilyl)amino)((trimethylsilyl)amino)borane (II) with Borane in Tetrahydrofuran. To a solution of II (15.93 g, 61.0 mmol) in 350 mL of ether was added $THF{\cdot}BH_3$ (65 mL, 65 mmol). After the reaction mixture was heated to reflux for 2.5 h, a white solid was filtered from the mixture and the solvent was removed by vacuum distillation. The remaining liquid was then separated into several crude fractions by vacuum distillation.

From the first fraction, bp 54 °C (80 torr), $(Me_3Si)_2NH$ (0.280 g, 2.8% yield based on II) and a second unidentified liquid were isolated by preparative-scale gas chromatography on column B at 110 °C. The IR spectrum of the second liquid contained the following characteristic absorption bands (cm^{-1}): 3160 (N–H); 2500 and 2450 (B–H). While the second fraction, bp 49–51 °C (60 torr), stood at room temperature for several weeks, IV (0.838 g, 14% yield based on II) precipitated. A vacuum distillation of the third fraction gave III (0.454 g, 4.3% yield based on II). Preparative-scale gas chromatography was used to isolate $(Me_3Si)_2HN_3B_3H_3$ (VI) (0.110 g, 2.4% yield based on II) from the fourth fraction on column B at 149 °C and V (1.524 g, 25% yield based on II) from the fifth fraction on column A at 173 °C.

Reaction of (Bis(trimethylsilyl)amino)chloro((trimethylsilyl)amino)borane (I) with Borane in Tetrahydrofuran. To a solution of I (29.63 g, 100 mmol) in 500 mL of ether was added $THF{\cdot}BH_3$ (100 mL, 100 mmol). After the solution had been heated to reflux for 2 h, a white solid was filtered from the mixture and the solvent was removed by vacuum distillation. The remaining liquid was separated into several fractions and an intractable tar by vacuum distillation.

While the first fraction, bp 48–49 °C (50 torr), stood at room temperature for 3 weeks, IV (0.366 g, 3.6% yield based on I) precipitated. From the second fraction, 40–43 °C (19 torr), $(Me_3Si)H_2N_3B_3H_3$ (VII) (0.191 g, 3.8% yield based on I) was isolated by preparative-scale gas chromatography on column A at 90 °C. A high-resolution mass spectrum of VII contained a molecular ion at *m/e* 153.1231 (calcd for $^{12}C_3{}^1H_{14}{}^{11}B_3{}^{14}N_3{}^{28}Si$: 153.1236). On column B at 146 °C VI (1.627 g, 22% yield based on I) was obtained from the third fraction and V (1.218 g, 12% yield based on I) was isolated from the fourth fraction on column A at 175 °C.

Synthesis of (Bis(trimethylsilyl)amino)borane (III). To a flask containing *n*-Bu_3SnH (11.20 g, 38.3 mmol) was added $(Me_3Si)_2NBCl_2$ (VIII) (4.846 g, 20.0 mmol). The stirred solution was heated to 44–45 °C for 85 min. At the end of this period no absorption at 1815 cm^{-1} (Sn–H) was observed in the IR spectrum of the solution.[11] Compound III (1.222 g, 35% yield based on VIII) was obtained from the reaction solution by vacuum distillation.

Warning! $(Me_3Si)_2NBH_2$ may ignite spontaneously on exposure to the atmosphere.

Reaction of (Bis(trimethylsilyl)amino)dichloroborane (VIII) with Lithium Tetrahydridoaluminate. To a mixture of $LiAlH_4$ (3.946 g, 104 mmol) in 400 mL of ether at 0 °C was added VIII (22.81 g, 94.5 mmol). After the flask was warmed to room temperature, the mixture was stirred for 30 min. The solid was then filtered from the mixture, and the solvent was removed from the filtrate by vacuum distillation. From the remaining liquid, III (4.789 g, 29% yield based on VIII) was distilled under vacuum. A second liquid (4.460 g), bp 89–92 °C (0.15 torr), was also isolated but could not be identified from its IR, ^1H NMR, and mass spectra.

Reaction of Hexamethyldisilazane with Borane in Tetrahydrofuran. To a flask of $(Me_3Si)_2NH$ (15.25 g, 94.3 mmol) at 0 °C was added $THF{\cdot}BH_3$ (95 mL, 95 mmol). After the flask had warmed to room temperature, the stirred solution was heated to 50 °C for a period

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(11) Newson, H. C.; Wood, W. G. *Inorg. Chem.* **1968**, *7*, 177.

Table III. Selected IR Data (cm^{-1})[a]

compd	ν(BH)	ν(NH)
$(Me_3Si)_2NB(H)N(H)SiMe_3$ (II)	2450 (m)	3400 (w)
$(Me_3Si)_2NBH_2$ (III)	2530 (m), 2450 (m)	
$[Me_3SiN(H)BH_2]_3$ (IV)	2310 (s, br), 2268 (s)	3155 (m)
$[Me_3SiNBH]_3$ (V)	2574 (w), 2487 (m)	
$(Me_3Si)_2HN_3B_3H_3$ (VI)	2500 (m), 2480 (m)	3440 (w)
$(Me_3Si)H_2N_3B_3H_3$ (VII)	2500 (m), 2490 (m)	3460 (m)

[a] Spectra were observed as neat liquids or KBr disks (intensity: w, weak; m, medium; s, strong; br, broad).

of 4 h and then heated to reflux for a few minutes before cooling to room temperature. The tetrahydrofuran was removed by vacuum distillation, and the remaining liquid was stored for 2 weeks at room temperature.

A vacuum distillation afforded three fractions: a liquid, bp 59–67 °C (85 torr), from which IV (0.174 g, 1.8% yield based on $(Me_3Si)_2NH$) precipitated after 18 days; III (0.834 g, 4.5% yield based on $(Me_3Si)_2NH$); n-$BuOB(H)N(SiMe_3)_2$[12] (2.208 g, 9.5% yield based on $(Me_3Si)_2NH$).

Results and Discussion

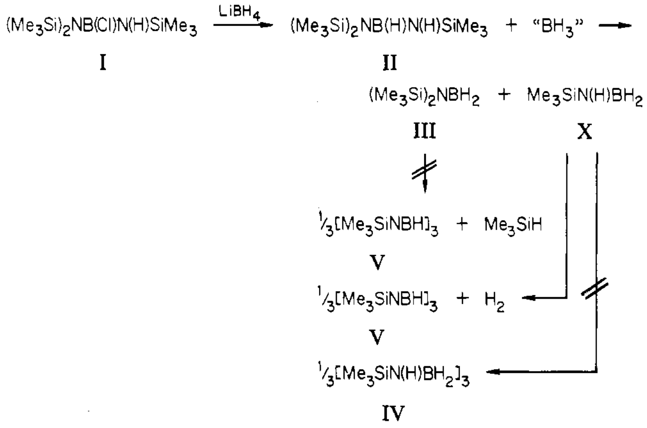
In an initial attempt to prepare (bis(trimethylsilyl)amino)((trimethylsilyl)amino)borane (II) via the reduction of (bis(trimethylsilyl)amino)chloro((trimethylsilyl)amino)borane (I) with $LiBH_4$, only 1,3,5-tris(trimethylsilyl)cyclotriborazane (IV) and 1,3,5-tris(trimethylsilyl)borazine (V) were isolated.[13] On further investigation of this reaction bis(trimethylsilyl)aminoborane (III) was also found along with IV and V (eq 1). In every case IV slowly crystallized from

$$\underset{\text{I}}{(Me_3Si)_2NB(Cl)N(H)SiMe_3} \xrightarrow{LiBH_4} \underset{\text{III}}{(Me_3Si)_2NBH_2} + \underset{\text{IV}}{[Me_3SiN(H)BH_2]_3} + \underset{\text{V}}{[Me_3SiNBH]_3} \qquad (1)$$

a clear colorless liquid which was a low-boiling distillate from the reaction mixture, and compounds III and V are clear colorless liquids. Compound V has been obtained previously from the reaction of hexamethyldisilazane and diborane.[14]

To explain the unexpected products in eq 1, we proposed the reaction pathway in Scheme I for the following reasons. Since BH_4^- readily reduces B–Cl bonds,[5,6] it would seem reasonable to assume that II is initially formed but immediately undergoes a further reaction. One such reaction could involve the cleavage of one of the B–N bonds in II by the borane moiety (BH_3) which is generated in the initial reduction of I. Indeed, (dialkylamino)boranes have been obtained from the reaction of diborane with bis(dialkylamino)boranes in ether when the alkyl substituents are larger than a methyl group.[18] Regardless of which B–N bond is cleaved, the products would be III and ((trimethylsilyl)amino)borane (X). The formation of V then could be explained by dehydrogenation and condensation of X in a manner similar to the preparation of the N-alkylborazines from (alkylamino)boranes.[19] However, because of the ease with which Si–N bonds are cleaved in silylamine–borane,[14] the elimination of trimethylsilane from III and condensation is an equally plausible approach to V. While trimerization of X would result in the formation of IV, Beachley has shown that the formation of the 1,3,5-trimethylcyclotriborazane proceeds through ionic intermediates[20] and similar intermediates may be involved in the formation of IV.

Scheme I. Proposed Pathway for the Reaction of $(Me_3Si)_2NB(Cl)N(H)SiMe_3$ with $LiBH_4$



In order to test the validity of the proposed reaction path, we attempted to synthesize the possible intermediates. These compounds were then allowed to undergo reactions which were dictated by the proposed steps, and identification of the expected products was taken as support for the proposed steps.

The first intermediate to be prepared was II. Compound II and $LiBH_4$ were obtained in low yields from the reaction of I and $LiAlH_4$. The low yield of II is probably due in part to the ease with which Si–N bonds are reduced by $LiAlH_4$.[21] Following Scheme I compound II was allowed to react with $THF{\cdot}BH_3$ in an ether solution. In addition to III, IV, and V, 1,3-bis(trimethylsilyl)borazine (VI) and hexamethyldisilazane were also isolated (eq 2). The yields of III, IV, and V are

$$\underset{\text{II}}{(Me_3Si)_2NB(H)N(H)SiMe_3} \xrightarrow{THF{\cdot}BH_3} \underset{\text{III}}{(Me_3Si)_2NBH_2} + \underset{\text{IV}}{[Me_3SiN(H)BH_2]_3} + \underset{\text{V}}{[Me_3SiNBH]_3} + \underset{\text{VI}}{(Me_3Si)_2HN_3B_3H_3} + (Me_3Si)_2NH \qquad (2)$$

reasonably similar to those which were obtained in the reaction of I with $LiBH_4$ (eq 1). These results support the presence of II and the borane species as intermediates in Scheme I. Likewise, the isolation of III in this reaction as well as the reaction of I with $LiBH_4$ points to the cleavage of one of the B–N bonds in II by the borane species as the second step in the reaction path.

Two potential routes to V exist in Scheme I. One involves III as a precursor and the other, X. Compound III was prepared by allowing (bis(trimethylsilyl)amino)dichloroborane (VIII) to react with tributyltin hydride or $LiAlH_4$. To determine if III would undergo elimination of trimethylsilane and condensation to form V, we heated a sample of III to 98–99 °C for 12 h. At the end of this period 75% of III was recovered, leaving an intractable tar. Thus, it would appear that III is not the precursor to V under the observed experimental conditions of these reduction reactions.

Although a sample of X could not be synthesized, results from a second study[12] also point to X as the precursor to both V and VI. In addition, difluoro((trimethylsilyl)amino)borane has been proposed as the precursor to a series of B-fluoroborazines analogous to compounds V, VI, and VII.[22] The formation of V from X probably proceeds through an ionic mechanism similar to those proposed for the formation of

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(12) Nutt, W. R.; Wells, R. L. *Inorg. Chem.*, following paper in this issue.

(13) Collins, A. L. Ph.D. Dissertation, Duke University, Durham, NC, 1966.

(14) Nöth, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1961**, *16B*, 618.

(15) Ito, K.; Watanabe, H.; Kubo, M. *J. Chem. Phys.* **1960**, *32*, 947.

(16) Ito, K.; Watanabe, H.; Kubo, M. *J. Chem. Phys.* **1961**, *34*, 1043.

(17) Beachley, O. T., Jr. *Inorg. Chem.* **1969**, *8*, 981.

(18) Keller, P. C. *J. Am. Chem. Soc.* **1974**, *96*, 3078.

(19) Hough, W. V.; Schaeffer, G. W.; Dzurus, M.; Stewart, A. C. *J. Am. Chem. Soc.* **1955**, *77*, 864.

(20) Beachley, O. T., Jr. *Inorg. Chem.* **1967**, *6*, 870.

(21) Cass, R.; Coates, G. E. *J. Chem. Soc.* **1952**, 2347.

(22) Elter, G.; Glemser, O.; Herzog, W. *Chem. Ber.* **1972**, *105*, 115.

1,3,5-trimethylborazine[23] and borazine.[24] Such a mechanism is particularly attractive since it offers a plausible explanation for the presence of small amounts of VI. During ring closure of the linear trimer, elimination of trimethylsilane might be favored in some cases rather than dehydrogenation. In such cases the further dehydrogenation of the cyclic intermediate would result in VI.

There is also the possibility that the second step of the pathway might involve a reaction between the borane species and I rather than II. Indeed, IV, V, and VI were isolated from the reaction of I with THF·BH$_3$ along with 1-(trimethylsilyl)borazine (VII) (eq 3). However, the major product in

$$\underset{\mathrm{I}}{\mathrm{(Me_3Si)_2NB(Cl)N(H)SiMe_3}} \xrightarrow{\mathrm{THF{\cdot}BH_3}} \underset{\mathrm{IV}}{\mathrm{[Me_3SiN(H)BH_2]_3}} + \underset{\mathrm{V}}{\mathrm{[Me_3SiNBH]_3}} + \underset{\mathrm{VI}}{\mathrm{(Me_3Si)_2HN_3B_3H_3}} + \underset{\mathrm{VII}}{\mathrm{(Me_3Si)H_2N_3B_3H_3}} \quad (3)$$

this reaction was VI rather than V and III was noticeably absent. These results suggest that the second step in Scheme I is the predominant route to the products in the LiBH$_4$ reduction of I.

The larger yield of VI in the reaction between I and THF·BH$_3$ is thought to be the result of a secondary reaction involving V and hydrogen chloride. In this reaction one of the Si–N bonds in V is cleaved by hydrogen chloride[25] to yield VI and chlorotrimethylsilane. The fact that hydrogen chloride is generated in this type of reduction reaction was substantiated by the isolation of di-*sec*-butylamine hydrochloride from the reaction between THF·BH$_3$ and chlorodi-*sec*-butylamino((trimethylsilyl)amino)borane.[12] Likewise, cleavage of one of the Si–N bonds in VI by hydrogen chloride would result in the formation of VII.

The precursor to IV has not been identified. The absence of IV in the reaction of di-*sec*-butylamino((trimethylsilyl)amino)borane and THF·BH$_3$[12] indicates that the formation of IV is probably not the result of a simple association of X. An examination was made of the liquid from which the trimer precipitated in the reduction of II. The gas chromatogram of this liquid contained three major bands, and the band with the longest retention time was found to belong to hexamethyldisilazane. All attempts to unambiguously characterize the compounds which were associated with the other bands were unsuccessful.

The presence of both hexamethyldisilazane and borane in these reactions raised the interesting question as to whether these compounds might be directly involved in the formation of IV. Previously, it was found that the reaction between hexamethyldisilazane and diborane produced a solid substance which on heating to 120 °C eliminated hydrogen and trimethylsilane to yield V.[14] Thus, it would seem quite possible that under a different set of experimental conditions only the elimination of trimethylsilane and the formation of IV might occur. Indeed, when hexamethyldisilazane was allowed to react with THF·BH$_3$, III, IV, and (bis(trimethylsilyl)amino)butoxyborane (IX) were obtained (eq 4). As had been

$$\mathrm{(Me_3Si)_2NH} \xrightarrow{\mathrm{THF{\cdot}BH_3}} \underset{\mathrm{III}}{\mathrm{(Me_3Si)_2NBH_2}} + \underset{\mathrm{IV}}{\mathrm{[Me_3SiN(H)BH_2]_3}} + \underset{\mathrm{IX}}{n\text{-}\mathrm{BuOB(H)N(SiMe_3)_2}} \quad (4)$$

observed in the earlier reduction reactions, IV crystallized from a low-boiling liquid fraction of the reaction mixture. The gas chromatogram of this liquid fraction also exhibited three bands, and the band with the longest retention time was found to belong to hexamethyldisilazane. In spite of the similarity in the experimental conditions under which IV is formed in this and the previous three reduction reactions, it is still not clear whether hexamethyldisilazane and the borane species are the intermediates leading to IV in eq 1.

The cleavage of a Si–N bond in preference to the N–H bond in hexamethyldisilazane by Lewis acids such as the borane species[14] and haloboranes[26] is well-known and has been used as an important synthetic tool to obtain many boron–nitrogen compounds. Consequently, the isolation of III from the above reaction (eq 4) is of significance since it indicates that the N–H bond of hexamethyldisilazane can be cleaved by a Lewis acid in preference to the Si–N bond under certain experimental conditions. Previously, it was found that dehydrohalogenation rather than cleavage occurred in the reaction between hexamethyldisilazane and triethylamine–trichloroborane.[8]

The formation of IX in the reaction involving hexamethyldisilazane and THF·BH$_3$ is thought to result from a disproportionation reaction between III and tributoxyborane. It is quite likely that during the reaction some tributoxyborane is formed since it may be obtained by heating the THF·BH$_3$ adduct to 64 °C.[27] Also preliminary evidence indicates that III does not react with tetrahydrofuran under the experimental conditions of the above reaction (eq 4), but IX was identified in the residue from a reaction between III and THF·BH$_3$.

The 1,3,5-trimethylcyclotriborazane has been found to exist in two isomeric forms.[28,29] The cis isomer in which the boron–nitrogen ring is thought to occupy a chair conformation with all methyl groups in equatorial positions is less volatile than the trans isomer which contains one methyl group in an axial position and the other two methyl groups in equatorial positions. However, in the case of the 1,3,5-tri-*tert*-butylcyclotriborazane, the trans isomer has been found to be less volatile than the cis isomer. This has led to the proposal that the trans isomer occupies a distorted-boat conformation in which the substituents are more exposed than in the chair conformation of the cis isomer and thus stronger interaction between neighboring molecules could occur.[29] In all cases where isolation of the two possible isomers of IV was attempted by means of sublimation, only one sublimate was obtained. The melting point and ^{1}H NMR spectrum of the sublimate were always similar to those of IV prior to sublimation. The ^{1}H NMR spectrum of IV contained two singlets in the ratio of 1:2. On the basis of these results, it would appear that the trans configuration is the only isomeric form to crystallize from the liquid. A molecular model of IV indicates that the steric interactions of the trimethylsilyl groups were smallest when the boron–nitrogen ring occupies a distorted-boat conformation.

One of the rather interesting aspects of this study has been the inability to observe ^{11}B–H coupling in the NMR spectra of these silicon–nitrogen–boron compounds with the exception of IV. Only a single broad band was found in the ^{11}B NMR spectra of V ane VI, and ^{1}H NMR spectra also exhibited a broad singlet (Table II) for the ^{11}B–H resonance. However, a symmetrical doublet was reported for the ^{11}B signal of borazine and the *N*-methylborazines, and a quartet was obtained for the ^{11}B–H resonance in the corresponding ^{1}H NMR spectra.[15-17] Likewise, while ^{11}B–H coupling was not discernible in the ^{1}H and ^{11}B NMR spectra of III in this study, a triplet was observed by others in the ^{11}B NMR spectra of

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[23] Beachley, O. T., Jr. *Inorg. Chem.* **1968**, *7*, 701.

[24] Niedenzu, K.; Blick, K. E.; Boenig, L. A. *Z. Anorg. Allg. Chem.* **1972**, *387*, 107.

[25] Fessenden, R.; Fessenden, J. S. *Chem. Rev.* **1961**, *6*, 361.

[26] Niedenzu, K.; Dawson, J. W. "Boron-Nitrogen Compounds"; Springer-Verlag: New York, 1965; p 56.

[27] Kollonitsch, J. *J. Am. Chem. Soc.* **1961**, *83*, 1515.

[28] Gaines, D. F.; Schaeffer, R. *J. Am. Chem. Soc.* **1963**, *85*, 395.

[29] Brown, M. P.; Heseltine, R. W.; Sutcliffe, L. H. *J. Chem. Soc. A* **1968**, 612.

methylene chloride solutions of III and (*tert*-butyl(trimethylsilyl)amino)borane,[30] and coupling was clearly present in the corresponding spectra of di-*sec*-butylaminoborane.[12]

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Registry No. I, 10078-93-0; II, 81121-65-5; III, 73452-31-0; IV, 81132-97-0; V, 17478-12-5; VI, 18134-91-3; VII, 81121-66-6; VIII, 6591-26-0; $(Me_3Si)_2NH$, 999-97-3; *n*-$BuOB(H)N(SiMe_3)_2$, 81121-58-6; $LiBH_4$, 16949-15-8; $THF\cdot BH_3$, 14044-65-6.

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[30] Wisian-Neilson, P.; Martin, D. R. *J. Inorg. Nucl. Chem.* **1979**, *41*, 1545.

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Reactions of ((Organosilyl)amino)(alkylamino)boranes with Selected Hydrides[1]

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Reductions of ((organosilyl)amino)(alkylamino)boranes with selected hydrides were studied in order to further clarify the reaction pathway of reactions between $LiBH_4$ and chlorobis(amino)boranes which contained an (organosilyl)amino group. A clear liquid which was identified as a mixture of *s*-Bu_2NBH_2 and $(Me_3Si)_2NBH_2$ was obtained from a reaction between *s*-$Bu_2NB(Cl)N(SiMe_3)_2$ and $LiBH_4$. The reaction of *s*-$Bu_2NB(H)N(SiMe_3)_2$ with $THF\cdot BH_3$ resulted in the formation of *n*-$BuOB(H)N(SiMe_3)_2$ and *s*-Bu_2NBH_2. The compounds *s*-$Bu_2NB(Cl)N(SiMe_3)_2$ and *s*-$Bu_2NB(H)N(SiMe_3)_2$ were prepared by allowing $(Me_3Si)_2NLi$ to react with *s*-Bu_2NBCl_2 and *s*-Bu_2NBClH, respectively. The compound *s*-Bu_2BClH was isolated from a reaction involving *s*-Bu_2NBCl_2 and $LiBH_4$ in a 1:1 mole ratio. In the reaction between *s*-$Bu_2NB(Cl)N(H)SiMe_3$ and $LiBH_4$, *s*-Bu_2NBH_2, $(Me_3Si)_2HN_3B_3H_3$, and $[Me_3SiNBH]_3$ were isolated. The same products were obtained from the reaction of *s*-$Bu_2NB(H)N(H)SiMe_3$ with $THF\cdot BH_3$. However, *s*-Bu_2NBH_2, *s*-Bu_2NBClH, and *s*-Bu_2NH_2Cl were isolated from the reaction of *s*-$Bu_2NB(Cl)N(H)SiMe_3$ with $THF\cdot BH_3$. The compounds *s*-$Bu_2NB(Cl)N(H)SiMe_3$ and *s*-$Bu_2NB(H)N(H)SiMe_3$ were prepared by allowing $(Me_3Si)_2NH$ to react with *s*-Bu_2NBCl_2 and *s*-Bu_2NBClH, respectively.

Introduction

In the previous paper it was reported that $(Me_3Si)_2NBH_2$, $[Me_3SiN(H)BH_2]_3$, and $[Me_3SiNBH]_3$ were isolated from the reaction of $(Me_3Si)_2NB(Cl)N(H)SiMe_3$ with $LiBH_4$. In order to explain the presence of these unexpected products, we proposed that initially $(Me_3Si)_2NB(H)N(H)SiMe_3$ was obtained along with B_2H_6 but that these two products underwent a further reaction. The isolation of $(Me_3Si)_2NBH_2$ suggested that this second reaction involved the cleavage of one of the B–N bonds in the bis(amino)borane by the borane species. The other product of this second reaction would be $Me_3SiN(H)BH_2$, which is thought to be the precursor to $[Me_3SiNBH]_3$. This proposition was supported by the fact that $(Me_3Si)_2NBH_2$, which is also a potential precursor to $[Me_3SiNBH]_3$, was found to be thermally stable under the experimental conditions of the reduction reaction. Despite an examination of the liquid from which $[Me_3SiN(H)BH_2]_3$ crystallized, it was not possible to identify the precursors to this compound.[2]

The results of this study raised the question as to whether other chlorobis(amino)boranes containing an (organosilyl)amino group would undergo the same type of reaction with $LiBH_4$. In order to answer this question, we allowed both *s*-$Bu_2NB(Cl)N(SiMe_3)_2$ and *s*-$Bu_2NB(Cl)N(H)SiMe_3$ to react with $LiBH_4$. Also, the reactions between $THF\cdot BH_3$ and both *s*-$Bu_2NB(H)N(SiMe_3)_2$ and *s*-$Bu_2NB(H)N(H)SiMe_3$ were investigated.

The purpose in selecting these compounds for the study was twofold. First, if cleavage of a B–N bond in the bis(amino)borane by the borane species does occur, then *s*-Bu_2NBH_2 would be formed. Since this compound may be easily isolated from the reaction mixture by vacuum distillation,[3] it would serve as an effective indicator for the occurrence of such a reaction. Second, the isolation of either or both $[Me_3SiN(H)BH_2]_3$ and $[Me_3SiNBH]_3$ from one of the above reactions would indicate clearly whether $(Me_3Si)_2NBH_2$ or $Me_3SiN(H)BH_2$ is involved in the formation of the six-membered boron–nitrogen ring system.

Experimental Section

Materials and General Procedures. The equipment and chemicals used in this study are described in the previous paper.[2] Di-*sec*-butylamine was obtained from K and K Laboratories, Inc., Plainview, NY, and Virginia Chemicals, Inc., West Norfolk, VA, and was distilled from calcium hydride prior to use. Dichloro(di-*sec*-butylamino)borane (I) was prepared by the procedure described in the literature.[4] An authentic sample of di-*sec*-butylamine hydrochloride (mp 121–122 °C) was prepared by passing hydrogen chloride through a pentane solution of di-*sec*-butylamine.

Reaction of Dichloro(di-*sec*-butylamino)borane (I) with Lithium Tetrahydroborate in a 1:2 Mole Ratio. The same reaction apparatus which was described previously[2] was used with the exception that a trap with two vacuum stopcocks was placed between the Friedrich condenser and bubbler. The trap was cooled to −196 °C. To a stirred mixture of $LiBH_4$ (5.338 g, 244 mmol) in 250 mL of ether was added *s*-Bu_2NBCl_2 (22.97 g, 110 mmol), and immediately a vigorous exothermic reaction occurred. When the reaction mixture ceased to boil, it was heated to reflux for 3 h.

From the volatile material collected in the trap, diborane (vp 219 torr (−112 °C), lit. vp 225 torr (−112 °C)[5]) was isolated by means of vacuum line techniques and identified from its IR spectrum.[6]

A white solid was filtered from the reaction mixture, and the solvent was removed from the filtrate by vacuum distillation. From the remaining liquid, *s*-Bu_2NBH_2 (II) was distilled as a colorless liquid (5.459 g, 36% yield based on I) and *s*-Bu_2NBClH (III) was isolated as a colorless liquid (2.736 g, 14% yield based on I).

Reaction of Dichloro(di-*sec*-butylamino)borane (I) with Lithium Tetrahydroborate in a 1:1 Mole Ratio. To a mixture of $LiBH_4$ (3.383 g, 155 mmol) in 500 mL of ether at 0 °C was added I (33.38 g, 159

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[1] Taken from: Nutt, W. R. Ph.D. Dissertation, Duke University, Durham, NC, 1971.

[2] Nutt, W. R.; Wells, R. L. *Inorg. Chem.*, preceding paper in this issue.

[3] Köster, R.; Bellut, H.; Hattori, S. *Justus Liebigs Ann. Chem.* **1968**, *720*, 1.

[4] Niedenzu, K.; Dawson, J. W. *J. Am. Chem. Soc.* **1959**, *81*, 5551.

[5] Shriver, D. F.; "The Manipulation of Air-Sensitive Compounds"; McGraw-Hill: New York, 1969; p 266.

[6] "Documentation of Molecular Spectroscopy", Institut für Spektrochemie und Angewandte Spektroskopie and DMS Scientific Advisory Board; Butterworths: London, 1967; Inorg. Card No. 146.

0020-1669/82/1321-2473$01.25/0