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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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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mmol). After the flask had warmed to room temperature, the mixture was stirred for 4 h. The solid was then filtered from the reaction mixture, and the solvent was removed from the filtrate by vacuum distillation. From the remaining liquid, III (17.29 g, 62% yield based on I) was distilled under vacuum.

Synthesis of (Di-*sec*-butylamino)borane (II). To a stirred mixture of $LiAlH_4$ (1.728 g, 45.4 mmol) in 250 mL of ether was added I (10.88 g, 52.0 mmol), and immediately an exothermic reaction occurred. When the reaction mixture ceased to boil, it was heated to reflux for 4 h. A gray solid was filtered from the reaction mixture, and the solvent was removed from the filtrate by vacuum distillation. From the remaining liquid, II (3.400 g, 46% yield based on I) was distilled under vacuum.

Synthesis of (Bis(trimethylsilyl)amino)chloro(di-*sec*-butylamino)borane (IV). The compound $s\text{-}Bu_2NB(Cl)N(SiMe_3)_2$ was prepared by means of a procedure similar to that described by Geymayer and Rochow.[7] To a solution of I (59.06 g, 282 mmol) in 150 mL of ether at −78 °C was added a slurry of $(Me_2Si)_2NLi$ (46.23 g, 277 mmol) in ether. After the flask had warmed to room temperature, the reaction mixture was heated to reflux for 30 min. A white solid was filtered from the reaction mixture, and the solvent was removed from the filtrate by vacuum distillation. From the remaining liquid, I (26.26 g, 44% recovered) and IV (29.54 g, 31% yield based on I) were isolated by vacuum distillation.

Synthesis of (Bis(trimethylsilyl)amino)(di-*sec*-butylamino)borane (V). Compound III (16.14 g, 92.5 mmol) was added to a solution of $(Me_3Si)_2NLi$ (18.05 g, 108 mmol) in 300 mL of ether at 0 °C. After the reaction mixture had been heated to reflux for 3 h, a white solid was filtered and the solvent was removed from the filtrate by vacuum distillation. From the remaining liquid, $s\text{-}Bu_2NB(H)N(SiMe_3)_2$ (V) (21.28 g, 77% yield based on III) was distilled under vacuum.

Reaction of (Bis(trimethylsilyl)amino)chloro(di-*sec*-butylamino)borane (IV) with Lithium Tetrahydroborate. To a stirred mixture of $LiBH_4$ (1.723 g, 79 mmol) in 270 mL of ether was added IV (22.60 g, 68 mmol). After the mixture had been heated to reflux for 3 h, a white solid was filtered from the reaction mixture and the solvent was removed from the filtrate by vacuum distillation. From the remaining liquid, a liquid (2.546 g, bp 46–50 °C (15 torr)) which was identified as a mixture of II and $(Me_3Si)_2NBH_2$ (VI) from its IR and mass spectra, an unidentified liquid (0.521 g, bp 82–86 °C (0.25 torr)), and IV (10.23 g, 45% recovered) were isolated by vacuum distillation.

Reaction of (Bis(trimethylsilyl)amino)(di-*sec*-butylamino)borane (V) with Borane in Tetrahydrofuran. To a solution of V (20.07 g, 66.9 mmol) in 250 mL of ether at 0 °C was added $THF\cdot BH_3$ (75 mL, 75 mmol). After the reaction mixture was heated to reflux for 3.5 h, a white solid was filtered from the mixture and the solvent was removed by vacuum distillation. From the remaining liquid, II (2.988 g, 32% yield based on V), $n\text{-}BuOB(H)N(SiMe_3)_2$ (VII) (4.140 g, 25% yield based on V), and V (6.290 g, 31% recovered) were distilled under vacuum. The ^1H NMR spectrum of a neat sample of VII contained the signals (TMS) δ −0.06 (s, 18, Me_3Si), 0.69 (t, 4.0, CH_3), 1.23 (m, 4.8, CH_2CH_2), and 3.61 (t, 2.2, CH_2O).

Synthesis of Chloro(di-*sec*-butylamino)((trimethylsilyl)amino)borane (VIII). To a solution of $(Me_3Si)_2NH$ (61.5 mL, 294 mmol) in 500 mL of hexane was added I (61.87 g, 294 mmol). After the reaction mixture had been heated to reflux for 2.5 h, $s\text{-}Bu_2NH_2Cl$ (0.256 g, 0.5% yield based on I, mp 120–121 °C) was filtered from the mixture and identified from its IR spectrum. The solvent was removed from the filtrate by vacuum distillation, and $s\text{-}Bu_2NB(Cl)N(H)SiMe_3$ (VIII) (47.08 g, 61% yield based on I) was isolated from the remaining liquid by vacuum distillation. The sample of VIII contained a very small amount of $s\text{-}Bu_2NH_2Cl$. Despite the fact that this solid was filtered prior to the distillation of VIII, a small amount of white solid always sublimed over with the distillate. Consequently, when VIII was used in a reaction, the small amount of solid present was filtered from a sample of VIII just prior to use. The elemental analysis was obtained from a sample of VIII which had been recovered from a solution of hexane and triethylamine. This sample of VIII contained no solid after being distilled.

Synthesis of (Di-*sec*-butylamino)((trimethylsilyl)amino)borane (IX). To a solution of $(Me_3Si)_2NH$ (28 mL, 130 mmol) in 300 mL of hexane was added III (23.05 g, 132 mmol). After the reaction mixture had been heated to reflux for 2.5 h, $s\text{-}Bu_2NH_2Cl$ (0.025 g, 0.1% yield based on III) was filtered from the mixture. The solvent was removed from the filtrate by vacuum distillation, and $s\text{-}Bu_2NB(H)N(H)SiMe_3$ (IX) (17.99 g, 60% yield based on III) was distilled from the remaining liquid. An analytical sample of IX was obtained by means of preparative scale gas chromatography at 122 °C on a column which contained 13% Silicone 702 on 60/80 mesh Chromosorb W (10 ft × $^1/_4$ in.).

Reaction of Chloro(di-*sec*-butylamino)((trimethylsilyl)amino)borane (VIII) with Lithium Tetrahydroborate. 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 $LiBH_4$ (1.955 g, 89.4 mmol) in 450 mL of ether was added VIII (19.80 g, 75.2 mmol). After the reaction mixture had been heated to reflux for 3.5 h, the trap was removed from the reaction apparatus and attached to the vacuum line. The only volatile material to be isolated from the trap was a very small amount of ether. A white solid was filtered from the reaction mixture, and the solvent was removed from the filtrate by vacuum distillation. The remaining liquid was then separated into several crude fractions by vacuum distillation.

From the first fraction, II (2.536 g, 24% yield based on VIII) was distilled under vacuum. Preparative-scale gas chromatography was used to isolate $(Me_3Si)_2HN_3B_3H_3$ (X) (0.054 g, 1% yield based on VIII) from the second fraction on column B[2] at 159 °C and $(Me_3SiNBH)_3$ (XI) (2.012 g, 27% yield based on VIII) from the third fraction on column A[2] at 187 °C.

Reaction of (Di-*sec*-butylamino)((trimethylsilyl)amino)borane (IX) with Borane in Tetrahydrofuran. To a solution of IX (17.68 g, 77.3 mmol) in 400 mL of ether at 0 °C was added $THF\cdot BH_3$ (80 mL, 80 mmol). After the solution had been heated to reflux for 3.5 h, a white solid was filtered from the reaction mixture and the solvent was removed from the filtrate by vacuum distillation. The remaining liquid was separated into several fractions by vacuum distillation.

From the first fraction, II (3.671 g, 34% yield based on IX) was distilled under vacuum. Compound X (0.342 g, 5.9% yield based on IX) was isolated from the second fraction by preparative-scale gas chromatography on column B[2] at 172 °C and on column A[2] at 183 °C; XI (1.489 g, 19% yield based on IX) was obtained from the third fraction.

Reaction of Chloro(di-*sec*-butylamino)((trimethylsilyl)amino)borane (VIII) with Borane in Tetrahydrofuran. To a solution of VIII (25.34 g, 96.5 mmol) in 500 mL of ether at 0 °C was added $THF\cdot BH_3$ (100 mL, 100 mmol). After the solution had been heated to reflux for 3.5 h, $s\text{-}Bu_2NH_2Cl$, (1.590 g, 10% yield based on VIII) was filtered from the reaction mixture and the solvent was removed from the filtrate by vacuum distillation. From the remaining liquid, II (5.345 g, 39% yield based on VIII) and III (0.434 g, 2.6% yield based on VIII) were isolated by vacuum distillation.

Results and Discussion

In order to prepare a sample of (di-*sec*-butylamino)borane (II), we allowed dichloro(di-*sec*-butylamino)borane (I) to react with $LiBH_4$ in a 1:2 mole ratio. However, chloro(di-*sec*-butylamino)borane (III) was isolated from the reaction mixture in addition to II and diborane. From a similar reaction between dichloro(diethylamino)borane and $NaBH_4$, only (diethylamino)borane was reported to have been isolated.[9] In addition, if I was allowed to react with $LiBH_4$ in a 1:1 mole ratio at 0 °C, then only III was obtained. It was also possible to prepare II from the reaction of I with $LiAlH_4$ in a 1:1 mole ratio.

The ^{11}B NMR spectrum of II (Table II) indicates that only the monomeric species of II is present at room temperature. While (di-*iso*-pentylamino)borane has been found to dimerize at room temperature,[10] it would appear that in the case of II branching at the α-carbon of the alkyl groups has a sufficient steric requirement to prevent association.

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Table I. Boiling Point, Analytical, and Molecular Weight Data

		calcd (found)						
compd	bp, °C (torr)	% C	% H	% B	% Cl	% N	% Si	mol wt,[a] *m/e*
s-Bu_2NBH_2 (II)	45 (15)[b]	68.11	14.29	7.67		9.93		141.1689
		(68.19)	(14.34)	(7.45)		(9.93)		(141.1692)
s-Bu_2NBClH (III)	59 (6)	54.47	10.91	6.16	20.20	7.98		175.1299
		(54.76)	(11.39)	(6.21)	(20.20)	(7.98)		(175.1297)
s-$Bu_2NB(Cl)N(SiMe_3)_2$ (IV)	86–88 (0.25)	50.21	10.84	3.23	10.59	8.36	16.77	334.2199
		(50.16)	(11.35)	(3.36)	(10.86)	(8.08)	(16.94)	(334.2211)
s-$Bu_2NB(H)N(SiMe_3)_2$ (V)	75–76 (0.35)	55.97	12.41	3.60		9.32	18.71	300.2588
		(56.08)	(12.42)	(3.81)		(9.02)	(18.31)	(300.2584)
n-$BuOB(H)N(SiMe_3)_2$ (VII)	56–57 (1.2)	48.96	11.50	4.41		5.71	22.90	245.1802
		(49.01)	(11.62)	(4.71)		(5.79)	(22.83)	(245.1800)
s-$Bu_2NB(Cl)N(H)SiMe_3$ (VIII)	64–66 (0.55)	50.29	10.74	4.12	13.50	10.66	10.69	262.1803
		(50.34)	(11.01)	(5.69)	(14.45)	(10.99)	(10.61)	(262.1805)
s-$Bu_2NB(H)N(H)SiMe_3$ (IX)	70–72 (2.9)	57.88	12.80	4.74		12.27	12.30	228.2193
		(58.16)	(12.66)	(4.71)		(12.29)	(11.98)	(228.2198)

[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] Literature bp 51 °C (16 torr).[3]

Table II. ^1H[a] and ^{11}B[b] Nuclear Magnetic Resonance Spectra

compd	δ(Me_3Si)	δ($\mathit{CH_3}CH_2$)	δ($\mathit{CH_3}CH$)	δ($CH_3\mathit{CH_2}$)	δ(NH)	δ($CH_3\mathit{CH}$)	δ(BH)	δ(^{11}B)
s-Bu_2NBH_2 (II)		0.57 (t)	0.86 (d)	1.22 (m)		2.70 (sx)	4.2[f]	36.3[h] (t, J_{BH} = 120 Hz)
s-Bu_2NBClH (III)		0.71 (t)	0.97 (d), 1.04 (d)	1.32 (m)		3.83 (sx) 2.87 (sx)	4.8[g]	34.3 (d, J_{BH} = 155 Hz)
s-$Bu_2NB(Cl)N(SiMe_3)_2$ (IV)	0.08 (s)	0.75 (t)	1.12 (d)	1.53 (m)		3.34[c] (s)		33.3 (s)
s-$Bu_2NB(H)N(SiMe_3)_2$ (V)	−0.02 (s)	0.73 (t)	1.00 (d)	1.33 (m)		3.16[c] (s)	[d]	35.2 (s)
s-$Bu_2NB(Cl)N(H)SiMe_3$ (VIII)	0.03 (s)	0.75 (t)	1.02 (d)	1.34 (m)	2.12 (s)	3.20 (sx)		
s-$Bu_2NB(H)N(H)SiMe_3$ (IX)	−0.18 (s)	0.59 (t)	0.84 (d)	1.14 (m)	1.85[c] (s)	2.68[e]	[d]	28.9 (s)

[a] All spectra were obtained with neat liquids at ambient temperatures except compounds IV and V whose spectra were obtained at 99 and 70 °C, respectively. All chemical shifts were determined with respect to Me_4Si by tube interchange, and a negative value for the chemical shift indicates a upfield shift from Me_4Si: s = singlet, d = doublet, t = triplet, sx = sextet, and m = multiplet. [b] All spectra were obtained on neat liquid samples at ambient temperatures. 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 $Et_2O{\cdot}BF_3$. The signals for compounds IV, V, and IX were quite broad (400–600 Hz). [c] A broad band, which was barely discernible at a spectral amplitude which put the C–H resonances on scale, was observed. [d] No signal was observed at spectral amplitudes which put the C–H resonances off scale. [e] An unresolved sextet was found. [f] While no signal was distinguishable at spectral amplitudes which put the C–H resonances on scale, the two downfield B–H resonances of the quartet were found at δ = 5.2 and 7.0 on amplification of the spectrum. The two upfield B–H resonances were masked by the C–H resonances. The chemical shift for the quartet was calculated with ^{11}B–H coupling constant obtained from the ^{11}B NMR spectrum. [g] No signal was discernible at spectrum amplitudes which put the C–H resonances on scale, but at higher amplitudes the two downfield B–H resonances of the quartet were observed at δ = 6.0 and 8.3. However, the upfield B–H resonances of the quartet were masked by the C–H resonances. The chemical shift of the quartet was calculated with the ^{11}B–H coupling constant obtained from the ^{11}B NMR spectrum. [h] δ = 36.6.[8]

In the ^1H NMR spectrum of III (Table II), the di-*sec*-butyl groups are found to be magnetically nonequivalent. This phenomenon could be the result of a barrier to rotation about the B–N bond.[11,12] Also, in a double resonance study when the sextet at δ 3.83 was radiated, the doublet at δ 0.97 collapsed and the doublet at δ 1.04 became a singlet when the sextet at δ 2.87 ppm was radiated.

Chloro(di-*sec*-butylamino)borane (III) is not the first chloro(dialkylamino)borane to be prepared. Examples of this type of compound were isolated when a series of bis(dialkylamino)boranes were allowed to react with 2 mol of hydrogen chloride.[13] However, the preparation of III from the reaction of I and $LiBH_4$ is significant since it offers a simple procedure for obtaining chloro(dialkylamino)boranes in large quantities. As the reactions of III with lithium bis(trimethylsilyl)amide and hexamethyldisilazane indicate, the chloro(dialkylamino)borane is an important synthetic reagent. Consequently, with the accessibility of this reagent which the reduction reaction offers, it is now possible to readily prepare large quantities of substituted monoaminoboranes, which are difficult to prepare by conventional methods, by means of dehydrohalogenation, cleavage, or metalation reactions.

Geymayer and Rochow observed that (bis(trimethylsilyl)amino)chloro(dialkylamino)boranes could be obtained easily by allowing sodium bis(trimethylsilyl)amide to react with dichloro(dialkylamino)borane.[7] Thus, the (bis(trimethylsilyl)amino)chloro(di-*sec*-butylamino)borane (IV) was prepared by allowing I to react with lithium bis(trimethylsilyl)amide. Likewise, the (bis(trimethylsilyl)amino)(di-*sec*-butylamino)borane (V) was isolated from the reaction of III with lithium bis(trimethylsilyl)amide.

When IV was allowed to react with $LiBH_4$, IV was recovered from the reaction mixture as well as a more volatile liquid. The IR and mass spectra of this liquid indicated that it was a mixture of II and (bis(trimethylsilyl)amino)borane (VI). However, because of the similarity in physical properties of II and VI, it was not possible to separate them by vacuum distillation. In addition, a third fraction was obtained from the reaction mixture but its components could neither be isolated nor characterized. Similarly, when V was allowed to react with $THF{\cdot}BH_3$, II, (bis(trimethylsilyl)amino)butoxyborane (VII), and V were isolated from the reaction mixture.

The presence of II and VI as products of the reaction between IV and $LiBH_4$ suggests a two-step reaction path. Initially, IV is thought to be reduced to V (eq 1), which then

$$\underset{\text{IV}}{s\text{-}Bu_2NB(Cl)N(SiMe_3)_2} \xrightarrow{LiBH_4} \underset{\text{V}}{s\text{-}Bu_2NB(H)N(SiMe_3)_2} + \text{"}BH_3\text{"} \quad (1)$$

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undergoes a second reaction with the generated borane species of the first step (eq 2). The fact that V and the borane species

$$\mathrm{V} + \text{“}BH_3\text{”} \rightarrow \underset{\text{II}}{s\text{-}Bu_2NBH_2} + \underset{\text{VI}}{(Me_3Si)_2NBH_2} \tag{2}$$

are intermediates through which II and VI are formed in this reaction is substantiated by the reaction of V with THF·BH_3. Although VI was not isolated from the reaction mixture, the isolation of (bis(trimethylsilyl)amino)butoxyborane (VII) indicated that VI was formed. In the preceding paper[2] VII was found along with VI in the reaction between hexamethyldisilazane and THF·BH_3. Consequently, it was proposed that VII was the result of a disproportionation reaction between VI and one of the butoxyboranes generated from THF·BH_3.[14]

One of the B–N bonds in bis(dialkylamino)borane has been found to be readily cleaved by diborane in ether to yield (dialkylamino)borane when the alkyl substituents are larger than a methyl group.[15] Thus, the reaction between V and the borane species probably involves the formation of an adduct by borane species with one of the nitrogens in V. Following the adduct formation, cleavage of the B–N bond containing the four-coordinate nitrogen atom occurs with a hydrogen transfer from the borane species. Regardless of which nitrogen in V is involved in the adduct formation, the products resulting from the cleavage of the B–N bond will be II and VI. However, on the basis of electronic considerations, the nitrogen of the di-*sec*-butylamino group would be predicted to be the stronger Lewis base of the two nitrogens in V; and the predominate reaction path is thought to involve the cleavage of the B–N bond containing the di-*sec*-butylamino group.

Since Si–N bonds are cleaved readily by haloboranes, substituted ((trimethylsilyl)amino)boranes can be prepared by allowing the substituted haloboranes to react with hexamethyldisilazane.[16] Chloro(di-*sec*-butylamino)((trimethylsilyl)amino)borane (VIII) was prepared from the reaction of I with hexamethyldisilazane. In a similar manner (di-*sec*-butylamino)((trimethylsilyl)amino)borane (IX) was obtained by allowing III to react with hexamethyldisilazane. A small amount of di-*sec*-butylamine hydrochloride was isolated in both reactions.

When VIII was allowed to react with $LiBH_4$, compounds II, X, and XI were isolated from the reaction mixture. The formation of these products is thought to result from the following sequence of reactions (eq 3–6). The isolation of II, X, and XI from the reaction mixture of IX and THF·BH_3 demonstrates that both the borane species and IX are intermediates in the reaction between VIII and $LiBH_4$. In addition, since diborane was not collected during the $LiBH_4$ reaction, it would appear that once formed the borane species undergoes further reaction. It will be recalled that in the reaction involving I with $LiBH_4$, diborane was isolated. While the reaction of VIII and the borane species could be postulated as an alternate source for the isolated products, the fact that II, III, and di-*sec*-butylamine hydrochloride were obtained from the reaction of VIII and THF·BH_3 discounts this possibility.

$$\underset{\text{VIII}}{s\text{-}Bu_2NB(Cl)N(H)SiMe_3} \xrightarrow{LiBH_4} \underset{\text{IX}}{s\text{-}Bu_2NB(H)N(H)SiMe_3} + \text{“}BH_3\text{”} \tag{3}$$

$$\mathrm{IX} + \text{“}BH_3\text{”} \rightarrow \underset{\text{II}}{s\text{-}Bu_2NBH_2} + \underset{\text{XII}}{Me_3SiN(H)BH_2} \tag{4}$$

$$3\mathrm{XII} \rightarrow \underset{\text{X}}{(Me_3Si)_2HN_3B_3H_3} + Me_3SiH + 2H_2 \tag{5}$$

$$3\mathrm{XII} \rightarrow \underset{\text{XI}}{(Me_3SiNBH)_3} + 3H_2 \tag{6}$$

The isolation of II from the reaction of IX with THF·BH_3 indicates that cleavage of one of the B–N bonds in IX by the borane species has occurred. This cleavage is thought to be preceded by the formation of an adduct between the borane species and the nitrogen of the B–N bond which is cleaved in IX. As noted previously, the products from this reaction are independent of the particular B–N bond cleaved; but it would appear on the basis of electronic considerations that the predominate path involves the cleavage of the B–N bond containing the di-*sec*-butylamino group.

The formation of the 1,3-bis(trimethylsilyl)borazine (X) and the 1,3,5-tris(trimethylsilyl)borazine (XI) in both the reaction of VIII and $LiBH_4$ and the reaction of IX with THF·BH_3 is quite significant. Since ((trimethylsilyl)amino)borane (XII) is the only other possible product of the cleavage reactions (eq 4) in addition of II, it must be assumed that XII is the precursor to both X and XI. The fact that N-substituted borazines can be prepared from monoaminoboranes was demonstrated earlier when 1,3,5-trimethylborazine was obtained from dimeric (methylamino)borane.[17]

The formation of X and XI is thought to proceed through an ionic mechanism similar to those proposed for the formation of 1,3,5-trimethylborazine[18] and borazine.[19] This type of mechanism is particularly attractive since it offers a plausible explanation for the presence of X. In view of the fact that cleavage of a Si–N bond in bis(trimethylsilyl)amine–borane has been observed,[20] it is possible that during ring formation from a linear trimer of XII elimination of trimethylsilane might be favored in some cases rather than dehydrogenation. Further dehydrogenation of the cyclic intermediate would yield X. Also, it is of interest to note that difluoro((trimethylsilyl)amino)borane has been suggested as the presursor to 1,3,5-tris(trimethylsilyl)-2,4,6-trifluoroborazine, 1,3-bis(trimethylsilyl)-2,4,6-trifluoroborazine, and 1-(trimethylsilyl)-2,4,6-trifluoroborazine.[21]

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Registry No. I, 81121-54-2; II, 22093-00-1; III, 81121-55-3; IV, 81121-56-4; V, 81121-57-5; VI, 73452-31-0; VII, 81121-58-6; VIII, 81121-59-7; IX, 81121-60-0; X, 18134-91-3; XI, 17478-12-5; $LiBH_4$, 16949-15-8; B_2H_6, 19287-45-7; $(Me_3Si)_2NLi$, 4039-32-1; THF·BH_3, 14044-65-6; $(Me_3Si)_2NH$, 999-97-3; *s*-Bu_2NH_2Cl, 626-23-3.

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