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Dehydrohalogenation and Cleavage Reactions in Silicon–Nitrogen–Boron Systems. Reactions of Bis(trimethylsilyl)aminotrimethylsilylaminochloroborane[1]

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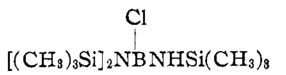
The reactions of bis(trimethylsilyl)aminotrimethylsilylaminochloroborane with ammonia, various amines, methyl alcohol, and *n*-butyllithium have been studied. A number of unsymmetrical trisaminoboranes, a methoxy compound, and a compound containing a four-membered boron–nitrogen ring have been prepared. Also, a possible mechanism for the formation of aminobis(trimethylsilyl)aminotrimethylsilylaminoborane from trichloroborane and excess hexamethyldisilazane is discussed.

Introduction

In a previous paper we reported that the reaction between hexamethyldisilazane and triethylamine–trichloroborane proceeds through a dehydrohalogenation reaction to give products which contain the bis(trimethylsilyl)amino group.[3] When these reactants are mixed in a 1:1 mole ratio, the reaction stops after the formation of bis(trimethylsilyl)aminodichloroborane (I); however, the addition of a second mole of the silicon amine results in cleavage of a silicon–nitrogen bond when a second boron–nitrogen bond is formed to give bis(trimethylsilyl)aminotrimethylsilylaminochloroborane (II).

$[(CH_3)_3Si]_2NBCl_2$

I



$[(CH_3)_3Si]_2N\overset{Cl}{\overset{|}{B}}NHSi(CH_3)_3$

II

Some reactions of II now have been investigated and in this paper we wish to describe these studies. As a part of these studies we have synthesized and characterized a series of unsymmetrically substituted trisaminoboranes, a class of compounds that has received attention in several papers in recent years.[4–10]

Experimental Section

Materials and Apparatus.—Compound II was prepared according to the procedure previously reported.[3] Elemental analyses, except where noted, were done by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. The boiling points are uncorrected. Infrared spectra were obtained using Perkin-Elmer 137 or 237 spectrophotometers. Proton nuclear magnetic resonance spectra were obtained using a Varian A-60 spectrometer and ^{11}B nuclear magnetic resonance spectra were obtained using a Varian HR-60 spectrometer with a 19.25-Mc radiofrequency probe. The tube interchange method of standardization was used in both cases with TMS = 0 as the standard for ^1H spectra and $(C_2H_5)_2O \cdot BF_3 = 0$ as the standard for ^{11}B spectra. Mass spectra were obtained using a Bendix Model 14 time-of-flight mass spectrometer. All reactions and manipulations were carried out in such a manner as to exclude moisture.

Aminobis(trimethylsilyl)aminotrimethylsilylaminoborane (III).—Anhydrous ammonia (1.2 ml at −80°, 58 mmoles) was bubbled into a solution of II (7.84 g, 26.6 mmoles) in 50 ml of dry hexane. The reaction mixture was refluxed for 30 min, then cooled and filtered under nitrogen. Fractional distillation of the filtrate gave a colorless liquid (2.29 g, 31% yield), bp 70° (2.0 mm), which gave an infrared spectrum identical with a spectrum of III which had been prepared by another method.[4]

When a sample of II (4.57 g, 15.5 mmoles) in 20 ml of dry benzene was refluxed with ammonium chloride (0.834 g, 15.6 mmoles) for 12 hr, III was not formed. The starting borane (II) was recovered in about 60% yield.

Methylaminobis(trimethylsilyl)aminotrimethylsilylaminoborane (IV).—Methylamine (1.8 ml at −80°, 45 mmoles), CP grade, was bubbled through a solution of II (5.09 g, 17.2 mmoles) in 50 ml of dry hexane at room temperature; then the reaction mixture was refluxed for 45 min. The white solid, methylammonium chloride (1.1 g, 95% yield), with an infrared spectrum identical with that of an authentic sample, was removed by vacuum filtration under dry nitrogen. Distillation of the filtrate gave a colorless liquid (3.94 g, 79% yield), bp 81–82° (2.0 mm).

Anal. Calcd for $C_{10}H_{32}BN_3Si_3$: C, 41.49; H, 11.14; B, 3.74; N, 14.52; Si, 29.11; mol wt, 289.5. Found: C, 41.28; H, 10.91; B, 3.75; N, 14.44; Si, 29.10; mol wt, 289 (mass spectrum).

Ethylaminobis(trimethylsilyl)aminotrimethylsilylaminoborane (V).—Ethylamine (2.7 ml, 42 mmoles), CP grade, was bubbled into a solution of II (5.73 g, 19.4 mmoles) in 50 ml of dry hexane. A white precipitate formed immediately. The mixture was refluxed for 1 hr, and then ethylammonium chloride (1.35 g, 85% yield), mp 105°, lit.[11] 109–110°, was removed by filtration. Distillation of the filtrate gave a colorless liquid (3.85 g, 66% yield), bp 85–86° (2.0 mm).

Anal. Calcd for $C_{11}H_{34}BN_3Si_3$: C, 43.53; H, 11.29; B, 3.56; N, 13.85; Si, 27.76; mol wt, 303.5. Found: C, 43.41; H, 11.38; B, 4.76, 3.42; N, 12.98, 13.23; Si, 27.50; mol wt, 303 (mass spectrum).

***t*-Butylaminobis(trimethylsilyl)aminotrimethylsilylaminoborane (VI).**—Freshly distilled *t*-butylamine (3.8 ml, 38 mmoles) in 50 ml of dry hexane was added dropwise to II (5.58 g, 18.9 mmoles) in 25 ml of hexane at room temperature. The reaction mixture was refluxed for 1 hr. *t*-Butylammonium chloride (1.99 g, 96% yield), mp 295°, lit.[12] 270–80°, was filtered from the mixture. Distillation of the filtrate gave a colorless liquid (4.49 g, 71% yield), bp 96–97° (2.0 mm).

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[1] Presented at the 153rd National Meeting of the American Chemical Society, Inorganic Division, Miami Beach, Fla., April 1967.

[2] Taken from the Ph.D. dissertation submitted by A. L. Collins to the Graduate School, Duke University, Durham, N. C.

[3] R. L. Wells and A. L. Collins, *Inorg. Chem.*, **5**, 1327 (1966).

[4] R. L. Wells and A. L. Collins, *Inorg. Nucl. Chem. Letters*, **2**, 201 (1966).

[5] D. W. Aubrey, W. Gerrard, and E. F. Mooney, *J. Chem. Soc.*, 1786 (1962).

[6] D. W. Aubrey, M. F. Lappert, and M. K. Majumdar, *ibid.*, 4088 (1962).

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[8] R. J. Brotherton and T. Buckman, *Inorg. Chem.*, **2**, 424 (1963).

[9] H. Jenne and K. Niedenzu, *ibid.*, **3**, 68 (1964).

[10] A. Kreutzberger and F. C. Ferris, *J. Org. Chem.*, **30**, 360 (1965).

[11] "Handbook of Chemistry and Physics," 46th ed, The Chemical Rubber Publishing Co., Cleveland, Ohio, 1965–1966.

[12] "Dictionary of Organic Compounds," Vol. 1, Oxford University Press, New York, N. Y., 1965.

Anal. Calcd for $C_{13}H_{38}BN_3Si_3$: C, 47.09; H, 11.55; B, 3.26; N, 12.67; Si, 25.42; mol wt, 331.6. Found: C, 47.00; H, 11.60; B, 4.80, 3.51; N, 12.41; Si, 24.67, 25.00; mol wt, 331 (mass spectrum).

Dimethylaminobis(trimethylsilyl)aminotrimethylsilylaminoborane (VII).—Dimethylamine (2.5 ml, 38 mmoles), CP grade, was bubbled into a solution of II (5.00 g, 17 mmoles) in 50 ml of dry hexane. The mixture was refluxed for 30 min. Dimethylammonium chloride (1.28 g, 93% yield), mp 172°, lit.[11] 170°, was removed by vacuum filtration. Fractional distillation of the filtrate gave a colorless liquid (3.82 g, 74% yield), bp 93–94° (2.0 mm).

Anal. Calcd for $C_{11}H_{34}BN_3Si_3$: C, 43.53; H, 11.29; B, 3.56; N, 13.85; Si, 27.76; mol wt, 303.5 Found: C, 43.59; H, 11.46; B, 3.44; N, 13.60; Si, 27.75; mol wt, 303 (mass spectrum).

Diethylaminobis(trimethylsilyl)aminotrimethylsilylaminoborane (VIII).—Diethylamine (3.7 ml, 36 mmoles) in 15 ml of dry hexane was added dropwise to a solution of II (5.23 g, 17.7 mmoles) in 35 ml of hexane at room temperature. The reaction mixture was refluxed for 1 hr. A white solid (1.74 g, 90% yield, based on diethylammonium chloride) was obtained by filtration. Distillation of the filtrate gave a colorless liquid (4.23 g, 72% yield), bp 105–107° (0.2 mm).

Anal. Calcd for $C_{13}H_{38}BN_3Si_3$: C, 47.09; H, 11.55; B, 3.26; N, 12.67; Si, 25.42; mol wt, 331.6. Found: C, 46.86; H, 11.54; B, 3.45; N, 12.64; Si, 25.11; mol wt, 331 (mass spectrum).

Bis(trimethylsilyl)aminobis(trimethylsilylamino)borane (IX). (a) **Reaction in Benzene.**—Bis(trimethylsilyl)aminotrimethylsilylaminochloroborane (II) (5.56 g, 18.9 mmoles) was placed in a 50-ml flask with a reflux condenser, and then hexamethyldisilazane (4 ml, 19.2 mmoles) in 20 ml of dry benzene was rapidly added. The reaction mixture was heated to reflux for 1 hr. The solvent was removed by distillation. Gas chromatographic analysis of the solvent fraction gave no indication of trimethylchlorosilane; therefore, it was assumed that no reaction occurred.

(b) **Reaction at 125°.**—The residue from the above reaction attempt was heated using an oil bath at 125° for 14 hr. Distillation at atmospheric pressure gave a fraction which was identified by its infrared spectrum as a mixture of trimethylchlorosilane and benzene. Distillation at reduced pressures yielded a colorless liquid (3.78 g, 57% yield), bp 89–95° (2.2 mm). An analytical sample of the product was obtained using preparative scale gas chromatography.

Anal. Calcd for $C_{12}H_{38}BN_3Si_4$: C, 41.46; H, 11.02; B, 3.11; N, 12.09; Si, 32.32; mol wt, 347.7. Found: C, 41.65; H, 11.06; B, 3.29; N, 12.19; Si, 32.53; mol wt, 347 (mass spectrum), 366 (cryoscopically in benzene).

(c) **From Aminobis(trimethylsilyl)aminotrimethylsilylaminoborane (III) and Trimethylchlorosilane.**—The borane (III) (3.3 g, 12 mmoles) was placed in a 50-ml flask which was connected to a vacuum line by a condenser. Triethylamine (2.5 ml, 18 mmoles) was dried over calcium hydride and condensed onto III. About 15 ml of freshly distilled trimethylchlorosilane was introduced into the vacuum line and transferred to a trap at −80°. Any hydrogen chloride present should have passed through the −80° trap into a −195° trap. The trimethylchlorosilane was then condensed into the reaction flask at −80°. Dry nitrogen was added to the system so that the total pressure was about 600 mm. The reaction mixture was refluxed for 132 hr, then filtered to remove triethylammonium chloride (0.11 g, 7% yield), mp 253°, lit.[11] 253–254°. The excess trimethylchlorosilane and triethylamine were removed from the reaction mixture leaving a colorless liquid which was mostly III; however, a small amount of the desired trisaminoborane (IX) was identified by gas chromatography.

Methoxybis(trimethylsilyl)aminotrimethylsilylaminoborane (X).—Methanol (0.64 ml, 16 mmoles) in 20 ml of dry acetone was added dropwise to a stirred solution of II (4.65 g, 15.8 mmoles) and triethylamine (2.2 ml, 16 mmoles) in 40 ml of acetone. The mixture was refluxed for 1 hr, then cooled and vacuum filtered under dry nitrogen. A white solid (2.13 g, 98% yield, based on triethylammonium chloride) was obtained. Distillation gave a slightly yellow liquid (1.89 g, 41% yield), bp 81–82° (2.0 mm).

Anal. Calcd for $C_{10}H_{31}BN_2OSi_3$: C, 41.35; H, 10.76; B, 3.73; N, 9.65; Si, 29.01; mol wt, 290.5. Found: C, 41.62; H, 10.81; B, 3.59; N, 9.62; Si, 29.93; mol wt, 290 (mass spectrum).

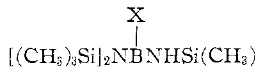
1,3-Trimethylsilyl-2,4-bis(trimethylsilyl)amino-1,3-diaza-2,4-diboretane (XI). (a) **Attempted Preparation from Bis(trimethylsilyl)aminotrimethylsilylaminochloroborane (II) and Triethylamine.**—A solution of II (5.45 g, 18.5 mmoles) and triethylamine (3.0 ml, 2.14 mmoles) in 59 ml of dry toluene was refluxed for 3.5 hr; then more triethylamine (2.0 ml, 14.2 mmoles) was added and the mixture was refluxed for 14 hr more. Triethylammonium chloride (0.18 g, 7.3% yield), mp 253°, lit.[11] 253–254°, was filtered from the system. The starting borane (II) was recovered (3.46 g, 63%) but XI could not be found.

(b) **Preparation from II Using *n*-Butyllithium.**—*n*-Butyllithium (11 ml of 1.6 *M*, 17.6 mmoles) was added to a stirred solution of II in 30 ml of dry hexane at 0°. The mixture was stirred at 0° for 30 min, then at room temperature for several hours. Distillation of the reaction mixture gave a colorless liquid (2.33 g, 44% yield), bp 71–74° (0.45 mm), and a solid residue. The liquid gave an infrared spectrum similar to the starting borane (II). A white solid (0.46 g, 10% yield) was obtained from the residue by sublimation, mp 196°, lit.[13] mp 212°, lit.[14] mp 208°. The pmr spectrum of XI in carbon tetrachloride contained two peaks, one at δ_1 0.18 ppm $\{[(CH_3)_3Si]_2N\}$ and the other at δ_2 0.13 ppm $[(CH_3)_3SiN]$, TMS = 0; lit.[13,14] δ_1 0.19, 0.20 ppm and δ_2 0.15, 0.16 ppm. The infrared spectrum of this solid was identical with a spectrum furnished by Dr. A. G. MacDiarmid of an authentic sample of XI. The analyses were done by Triangle Chemical Laboratories, Chapel Hill, N. C.

Anal. Calcd for $C_{18}H_{54}B_2N_4Si_6$: C, 41.83; H, 10.53; mol wt, 516.8. Found: C, 41.07; H, 10.29; mol wt, 516 (mass spectrum).

Results and Discussion

It has been found that compound II can be readily converted to unsymmetrical trisaminoboranes which contain three different amine groups. The reaction used to prepare compounds III–VIII was the amination of II using ammonia, a primary amine, or a secondary amine. All of these reactions proceeded readily at room temperature, as indicated by the formation of a precipitate at room temperature, and most of the trisaminoboranes were obtained in good yields after refluxing the reaction mixture in hexane. Another trisaminoborane, bis(trimethylsilyl)aminobis(trimethylsilylamino)borane (IX), was prepared by a cleavage reaction between II and hexamethyldisilazane. In this reaction it was necessary to heat the hexamethyldisilazane and II to 125°, in the absence of solvent, to effect the formation of IX; whereas II was obtained from hexamethyldisilazane and I in refluxing benzene.[3]



$$[(CH_3)_3Si]_2N\overset{\overset{\displaystyle X}{|}}{B}NHSi(CH_3)_3$$

III, X = NH_2
IV, X = $NHCH_3$
V, X = NHC_2H_5
VI, X = $NHC(CH_3)_3$
VII, X = $N(CH_3)_2$
VIII, X = $N(C_2H_5)_2$
IX, X = $NHSi(CH_3)_3$
X, X = OCH_3

The reaction of II with methanol and triethylamine indicates that alkoxy derivatives of this compound are as easily formed as the amino derivatives. Although only the methoxy compound (X) was prepared, the

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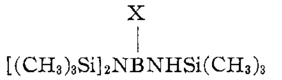
(13) C. R. Russ and A. G. MacDiarmid, *Angew. Chem. Intern. Ed. Engl.*, **3**, 509 (1964).

(14) P. Geymeyer, E. G. Rochow, and U. Wannagat, *ibid.*, **3**, 633 (1964).

TABLE I

$^{1}H^{a}$ AND $^{11}B^{b}$ NUCLEAR MAGNETIC RESONANCE SPECTRA OF

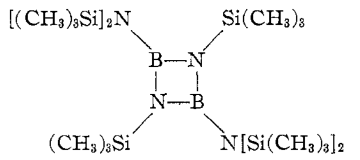


$$[(CH_3)_3Si]_2N\overset{X}{\overset{|}{B}}NHSi(CH_3)_3$$

X	δ($(CH_3)_3Si$)	δ(NHSi)	δ(NHR)	δ(CH_3)	δ(CH_2)	δ(^{11}B)
NH_2	−0.11	1.45	1.92			−28.5
$NHCH_3$	−0.08	1.40	2.03^{c} J = 6 cps	2.39^{d} J = 6 cps		−26.7
NHC_2H_5	−0.08	1.35	1.98^{e} J = 7 cps	0.85^{e} J = 7 cps	2.78^{f} J = 7 cps	−27.2
$NHC(CH_3)_3$	0.08, 0.10	1.75	2.37	1.16		−25.4
$N(CH_3)_2$	−0.10, −0.05	1.43		2.44		−28.0
$N(C_2H_5)_2$	−0.03, 0.00	1.53		0.86^{e} J = 7 cps	2.93^{c} J = 7 cps	−25.4
$NHSi(CH_3)_3$^{g}	0.05	1.71				−28.0
OCH_3	−0.10, −0.15	1.63		3.25		−27.5

[a] TMS = 0; negative values of δ (ppm) are upfield from the standard. [b] $(C_2H_5)_2O \cdot BF_3$ = 0; negative values of δ (ppm) are downfield from the standard. [c] Quartet. [d] Doublet. [e] Triplet. [f] Quintet. [g] Carbon tetrachloride solution; all other samples were prepared neat.

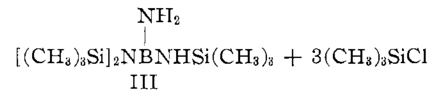
facility with which the dehydrohalogenation occurred suggests that other alkoxy derivatives could also be synthesized. The reaction of II with *n*-butyllithium resulted in the formation of the previously reported[13–15] compound 1,3-trimethylsilyl-2,4-bis(trimethylsilyl)-amino-1,3-diaza-2,4-diboretane (XI). An attempt to prepare XI using triethylamine with II was not successful.



XI

The ^{1}H and ^{11}B nuclear magnetic resonance spectra of the seven trisaminoboranes and the methoxy compound were obtained and these data are summarized in Table I. One observation concerning the ^{1}H spectra of three of the trisaminoboranes is the number of peaks which are attributed to the methyl protons on the trimethylsilyl groups. There were two peaks for these protons for compounds VI, VII, and VIII, but only one peak in the spectra of the other trisaminoboranes. In the cases where two peaks appeared it was impossible to determine accurately their relative ratio because of overlapping, but they appeared to be in a 2:1 ratio. A very similar situation in a series of organo-substituted and silyl-substituted aminoboranes has been reported recently by Geymeyer and Rochow.[15] It should also be noted that there was only one peak for trimethylsilyl protons in the spectrum of IX and two peaks for this type of proton in the spectrum of X.

The fact that II can be prepared and then converted to III by a reaction with ammonia gives some evidence for the sequence of reactions that may be taking place when III is formed directly from trichloroborane and excess hexamethyldisilazane[4]



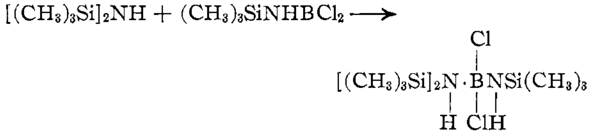
$$3[(CH_3)_3Si]_2NH + BCl_3 \longrightarrow [(CH_3)_3Si]_2N\overset{NH_2}{\overset{|}{B}}NHSi(CH_3)_3 + 3(CH_3)_3SiCl \quad (1)$$

III

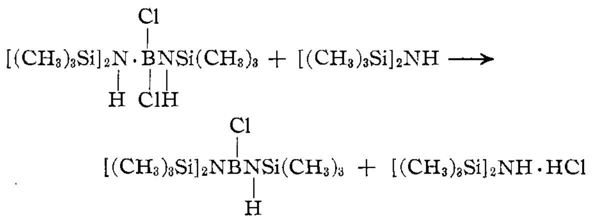
Thus, the formation of III in the above reaction can best be explained by a series of cleavage, dehydrohalogenation, and substitution reactions. The first step would be a cleavage of a silicon–nitrogen bond in hexamethyldisilazane by trichloroborane to give trimethylsilylaminodichloroborane as described by Becke-Goehring and Krill[16] and Andrianov,[17] *et al.*

$$[(CH_3)_3Si]_2NH + BCl_3 \longrightarrow (CH_3)_3SiNHBCl_2 + (CH_3)_3SiCl \quad (2)$$

The next reaction would be the formation of an adduct with hexamethyldisilazane to give bis(trimethylsilyl)-amine–trimethylsilylaminodichloroborane (eq 3). Although trimethylsilylaminodichloroborane is probably a weaker acid than trichloroborane, it is probably strong enough to form an adduct with the silicon amine. Hexamethyldisilazane is only a weak base, but it is probably a strong enough base to form a weakly associated adduct. It is perhaps the weakness of this dative bond that prevents silicon–nitrogen bond cleavage as in the first step. The third reaction is dehydrohalogenation between a silicon amine and a boron halide (eq 4). In the reaction under consideration the dehydrohalogenating agent is hexamethyldisilazane and the product is bis(trimethylsilyl)aminotrimethylsilylaminochloroborane (II). The other reaction product,



$$[(CH_3)_3Si]_2NH + (CH_3)_3SiNHBCl_2 \longrightarrow [(CH_3)_3Si]_2\underset{H}{\underset{|}{N}} \cdot \underset{Cl}{\underset{|}{\overset{Cl}{\overset{|}{B}}}}\underset{H}{\underset{|}{N}}Si(CH_3)_3 \quad (3)$$



$$[(CH_3)_3Si]_2\underset{H}{\underset{|}{N}} \cdot \underset{Cl}{\underset{|}{\overset{Cl}{\overset{|}{B}}}}\underset{H}{\underset{|}{N}}Si(CH_3)_3 + [(CH_3)_3Si]_2NH \longrightarrow [(CH_3)_3Si]_2N\overset{Cl}{\overset{|}{B}}\underset{H}{\underset{|}{N}}Si(CH_3)_3 + [(CH_3)_3Si]_2NH \cdot HCl \quad (4)$$

II

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(15) P. Geymeyer and E. G. Rochow, *Monatsh. Chem.*, **97**, 437 (1966).

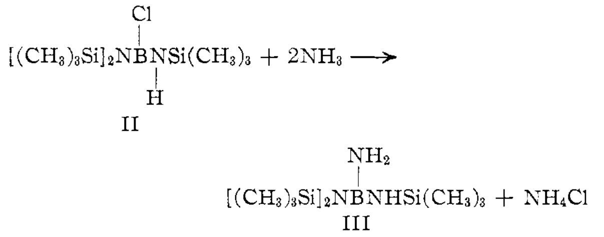
(16) M. Becke-Goehring and H. Krill, *Chem. Ber.*, **94**, 1059 (1961).

(17) K. A. Andrianov, V. V. Astakhin, and D. A. Kochkin, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1757 (1962).

bis(trimethylsilyl)ammonium chloride, is unstable and will spontaneously decompose into hexamethyldisilazane, trimethylchlorosilane, and ammonia (eq 5). The

$$[(CH_3)_3Si]_2NH \cdot HCl \longrightarrow \tfrac{1}{2}[(CH_3)_3Si]_2NH + (CH_3)_3SiCl + \tfrac{1}{2}NH_3 \quad (5)$$

ammonia produced in reaction 5 is necessary for the next reaction. This step is the amination of the remaining boron–chlorine bond to form aminobis(trimethylsilyl)-aminotrimethylsilylaminoborane (III) and ammonium chloride (eq 6). The large amino groups on the boron probably prevent any condensation to form a diborylamine. The disappearance of the ammonium chloride[4] in the reaction in which the ratio of the hexamethyldisilazane to trichloroborane was 3:1 can best be explained by the final step in the reaction sequence. This is the reaction of hexamethyldisilazane with ammonium chloride to form trimethylchlorosilane and ammonia. This is the reverse of the reaction in which hexamethyldisilazane is normally prepared; however, the reaction between a silyl halide and an amine has been found to be reversible by Anderson.[18] Since the ammonia formed can be constantly used in the formation of III (eq 6), the reverse of this last reaction in this scheme cannot occur readily (eq 7). The necessity of having an excess of hexamethyldisilazane for the formation of the trisaminoborane (III) was demonstrated by a reaction between hexamethyldisilazane and boron trichloride in a 1:1 mole ratio in refluxing hexane. In this experiment there was no evidence for the formation of III.



$$[(CH_3)_3Si]_2N\overset{Cl}{\underset{H}{B}}NSi(CH_3)_3 + 2NH_3 \longrightarrow [(CH_3)_3Si]_2N\overset{NH_2}{B}NHSi(CH_3)_3 + NH_4Cl \quad (6)$$

II

III

$$\tfrac{1}{2}[(CH_3)_3Si]_2NH + NH_4Cl \longrightarrow (CH_3)_3SiCl + \tfrac{3}{2}NH_3 \quad (7)$$

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(18) H. H. Anderson, *J. Am. Chem. Soc.*, **73**, 5802 (1951).

Contribution from Shionogi Research Laboratory,
Shionogi & Company, Ltd., Fukushima-Ku, Osaka, Japan

The Kinetics and Mechanisms of Hydrolysis of Borazine Derivatives in Aqueous Dioxane

By TAMOTSU YOSHIZAKI, HARUYUKI WATANABE, and TOSHIO NAKAGAWA

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The hydrolysis rates of B-tris(phenylethynyl)borazine derivatives are increased by the addition of acids and bases. The reaction was found to be first order with respect to borazine as well as with respect to acid and base concentrations. The isotope effect and the solvent isotope effect on the hydrolysis rate were measured to elucidate the mechanism. The hydrolysis proceeds more rapidly in dioxane–H_2O than in dioxane–D_2O solution by a factor of 2.1 for hydrochloric acid catalyzed hydrolysis and by a factor of 1.70 for triethylamine-catalyzed hydrolysis. The activation energies $\Delta E^{\ddagger}$ for the acid- and amine-catalyzed hydrolyses are about 10 kcal/mole for all of the derivatives examined. On the basis of these data, a model of the transition state was proposed for the acid- and base-catalyzed hydrolyses, respectively.

Introduction

While considerable attention has been paid to the solvolysis reactions of boron compounds in recent years, the great majority of the work has dealt with boron compounds involving an sp^3-hybridized boron atom, *e.g.*, borohydrides and amine boranes.[1–3] Few studies of the solvolysis of sp^2 boron–nitrogen compounds have been described, and no mechanistic studies of the hydrolyses of borazines have been made probably owing to "the complexities involved in considering possible hydrolysis mechanisms of these compounds."[4] It is the purpose of the present and the following papers to elucidate the mechanism of borazine hydrolysis and to ascertain the factors determining hydrolysis stability.

The borazine derivatives dissolved in inert organic solvents react with water quantitatively to produce the corresponding amines and boronic acids according to the over-all equation

$$(BRNR')_3 + 6H_2O \longrightarrow 3RB(OH)_2 + 3R'NH_2$$

In preliminary experiments to determine the experimental conditions, it was found that the hydrolysis rate was greatly increased by the addition of base and

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