TABLE III

N-TRIALKYLBORAZINE NMR DATA

Compd	τ^c	Area ratio	Multiplicity	J^c	Assignment
$(HBNC_2H_5)_3{}^a$	6.64 (6.66)	2.0	Quartet	7.0 (7.1)	N-C_2H_5 (methylene)
	8.90 (8.86)	3.0	Triplet	7.0 (7.1)	N-C_2H_5 (methyl)
$(HBN\text{-}i\text{-}C_3H_7)_3{}^a$	6.13 (6.33)	1.0	Septet	7.0 (7.0)	N-i-C_3H_7 (methyne)
	8.63 (8.77)	6.0	Doublet	7.0 (6.8)	N-i-C_3H_7 (methyl)
$(HBN\text{-}tert\text{-}C_4H_9)_3{}^b$	8.64 (8.63)	. . .	Singlet	. . . (. . .)	N-*tert*-C_4H_9

[a] Neat material (trace benzene as internal standard). [b] Concentrated solution in CH_2Cl_2 (CH_2Cl_2 standard). [c] Literature values are included in parentheses for comparison. Data from ref 13.

TABLE IV

MASS SPECTRAL DATA FOR N-TRIALKYLBORAZINES

$(HBNC_2H_5)_3$		$(HBN\text{-}i\text{-}C_3H_7)_3$		$(HBN\text{-}tert\text{-}C_4H_9)_3$	
m/e	Rel intens	m/e	Rel intens	m/e	Rel intens
165	8.9	207	1.25	249	1.29
164	11.2	192	93.7	234	100.0
163	4.9	191	66.2	233	70.5
162	2.3	190	20.6	232	10.2
150	100.0	189	5.63	231	1.29
149	73.5	165	6.25	178	42.3
148	25.0	164	7.50	177	28.6
147	3.2	150	92.6	176	5.13
93	4.5	149	70.0	100	18.0
79	6.6	148	20.0	93	25.8
78	27.4	147	4.38	92	3.84
77	10.9	79	16.3	58	88.5
63	4.9	78	100.0	57	25.8
52	9.9	77	27.5	53	1.29
51	9.2			52	2.56
50	8.2			51	1.29
39	4.3			50	1.29
38	6.0			44	25.8
37	3.3			42	25.8
				41	32.0
				39	12.8
				32	25.8
				28	60.4

ml) were heated at 120° under 3000 psi of hydrogen for 12 hr (reaction 3, Table I). The chamber was allowed to cool and was vented; the benzene-soluble material was separated from excess, unreacted aluminum by filtration in the drybox. Removal of solvent *in vacuo* left a white solid. The infrared spectrum of this material (Nujol mull) revealed ν(B–H) (2560 cm^{-1}), aromatic ν(C–H) (3100 cm^{-1}), weak ν(N–H) (3650 cm^{-1}), and other "fingerprint" frequencies. The weak ν(N–H) band indicates the presence of $H_nBN(H_{n-1})$-*tert*-C_4H_9 (n = 1 or 2) compounds in admixture with the expected N-tri-*tert*-butylborazine. This mixture was therefore heated at 200° for 2 hr to pyrolize any primary aminoborane contaminant. The infrared spectrum of the heated material did not exhibit a band in the 3650-cm^{-1} region, indicating complete pyrolysis. N-tri-*tert*-butylborazine was sublimed by heating the mixture at 80° (0.25 mm). It was difficult to obtain complete isolation of the borazine due presumably to its relatively low volatility under these conditions. Complete isolation required several sublimation attempts which involved mechanically "breaking up" the solid residue repeatedly in the drybox. The sublimed material obtained in these steps was combined and resublimed at 80° (0.25 mm); yield 7.15 g, 86%. The purity and identity of this product was determined by its melting point of 93° (lit.[15] mp 94°) and by infrared, proton magnetic resonance, and mass spectral analyses (Tables II–IV, respectively). The spectral data compare well with the literature values.[13,15] The mass spectrum of this solid revealed a weak molecular ion at m/e 249 and an intense M − 15 peak at m/e 234. The isotopic cluster for the M − 15 peak (relative intensities of m/e 231, 232, 233, and 234) was found to be 1.9: 17.1:70.3:100.0.

Results and Discussion

The reaction of primary, secondary, and tertiary monoalkylamines (alkyl = ethyl, isopropyl, and *tert*-butyl) with phenyl borate, aluminum, and hydrogen (3000 psig) in benzene solution proceeds to give the corresponding N-trialkylborazine in high yield (82–93%) according to the equation

$$B(OC_6H_5)_3 + Al + RNH_2 \xrightarrow[\Delta,\text{pressure}]{H_2} {}^1/_3(HBNR)_3 + Al(OC_6H_5)_3 \quad (7)$$

where R = C_2H_5, i-C_3H_7, and *tert*-C_4H_9.

The exact reaction conditions and product yields are summarized in Table I. According to this study, heating equimolar mixtures of phenyl borate and monoalkylamine with excess aluminum and hydrogen gives 82% yield of N-triethylborazine after 5 hr (reaction 1), 93% yield of N-triisopropylborazine, and 86% yield of N-tri-*tert*-butylborazine after 12 hr (reactions 2 and 3, respectively). The adopted procedure involves filtration of the reaction products (to remove excess, unreacted aluminum metal) followed by removal of the reaction solvent under vacuum and distillation (in the case of the ethyl and isopropyl compounds) or sublimation (in the case of the *tert*-butyl derivative) of the borazine product from by-product aluminum phenoxide. Although this by-product is normally insoluble in hydrocarbon solvents, it was found to be largely soluble in hydrocarbon solutions of a N-trialkylborazine.

A high-temperature digestion step was found necessary for synthesis of N-tri-*tert*-butylborazine prior to sublimation of this product (see Experimental Section for details) due to the presence of trace primary amine–borane impurities ($H_nBN(H_{n-1})$-*tert*-C_4H_9, n = 2 or 3) which persisted under conditions of the direct preparation reaction (120° for 12 hr). That these species are pyrolized only slowly to the borazine at these temperatures was demonstrated by direct pyrolysis of *tert*-butylamine–borane at ~100°.[15]

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[15] A. Meller and E. Schoschel, *Inorg. Nucl. Chem. Lett.*, **2**, 41 (1966).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
PAUL M. GROSS CHEMICAL LABORATORY,
DUKE UNIVERSITY, DURHAM, NORTH CAROLINA 27706

The Preparation of Bis(trimethylsilyl)aminochlorodimethylaminoborane[1]

BY HARVEY L. PAIGE AND RICHARD L. WELLS*

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The dehydrohalogenation reaction between triethylamine–trichloroborane and hexamethyldisilazane was

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[1] (a) Presented at the Southeastern Regional Meeting of the American Chemical Society, Tallahassee, Fla., Dec 1968. (b) Taken from the Ph.D. dissertation of H. L. Paige, Duke University, Durham, N. C., 1969.

reported by Wells and Collins.[2] Dialkylaminobis(trimethylsilyl)aminochloroboranes have been prepared by a metalation reaction where the alkyl group was ethyl, isopropyl, cyclohexyl, or phenyl.[3] It is now reported that the dehydrohalogenation reaction can be extended to produce the first member of the series, bis(trimethylsilyl)aminochlorodimethylaminoborane (I), by the reaction between hexamethyldisilazane and trimethylamine–dichlorodimethylaminoborane. The product is generally contaminated with another compound, bis(trimethylsilyl)aminobis(dimethylamino)borane (II), and, under some conditions, chlorobis(dimethylamino)borane is also observed. The study of II yielded an alternate synthetic route to I. Thus, II is synthesized from the lithium salt of hexamethyldisilazane[4] and chlorobis(dimethylamino)borane, and I is then synthesized from II by the cleavage of a dimethylamino moiety by hydrogen chloride.[5]

$[(CH_3)_3Si]_2NB(Cl)N(CH_3)_2$
I

$[(CH_3)_3Si]_2NB[N(CH_3)_2]_2$
II

Experimental Section

Materials and Apparatus.—Hexamethyldisilazane was purchased from the Dow-Corning Corp., Midland, Mich., and was distilled prior to use. Boron trichloride, dimethylamine, and trimethylamine were purchased from Matheson Co., East Rutherford, N. J., and were used without further purification. Some liquid products were purified using a Nester-Faust annular Teflon spinning-band column.

Elemental compositions were determined by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Routine mass spectra were obtained on a Bendix Model 14 time-of-flight mass spectrometer; routine pmr spectra were obtained on a Varian A-60 spectrometer and were referred to TMS = 0.0 by the tube interchange method of standardization. The ^{11}B nmr datum was obtained on a Varian HA-100 spectrometer and was referred to $(CH_3CH_2)_2O \cdot BF_3$ external standard. Infrared spectra were obtained on a Perkin-Elmer 137 or 237 spectrophotometer. Refractive indices were measured on a Bausch and Lomb Abbe-type refractometer. Melting points were determined by observing samples sealed in glass tubes suspended on a pentane thermometer in a cooling bath contained in an unsilvered dewar flask.

Tris(dimethylamino)borane was prepared according to the method reported in ref 6 with minor modifications to allow a larger scale preparation. Dichlorodimethylaminoborane was then prepared by disproportionation according to the method of Fritz,[7] again with minor modifications. The dichlorodimethylaminoborane was allowed to dimerize and was then washed with hexane, methanol, and water and then dried and left in this relatively inert form until ready for use.[8] Employing a different ratio of trichloroborane to tris(dimethylamino)borane, the method of Fritz was also used to prepare chlorobis(dimethylamino)borane.[9]

Preparation of Bis(trimethylsilyl)aminochlorodimethylaminoborane (I).—A. The difficulty in purifying and manipulating the trimethylamine adduct of dichlorodimethylaminoborane[8] required that an *in situ* preparation of the adduct be employed. Thus, in a typical experiment, a 500-ml flask containing a stirring bar was charged with 200 ml of benzene and attached to a manifold which allowed introduction of gases and liquids. In an atmosphere of dry nitrogen, the flask was cooled to −78° and the pressure was adjusted to 90 mm. A 29-g (0.23-mol) sample of the dichlorodimethylaminoborane dimer was then melted and distilled[10] directly into the cold reaction flask. Approximately 0.8 molar equiv of trimethylamine (0.18 mol, 11 g) was then condensed into the flask and the mixture was allowed to warm to room temperature. After stirring, the mixture was again cooled to −78° and 0.75 molar equiv of hexamethyldisilazane (0.14 mol, 22 g) in 75 ml of dry benzene was added. The mixture was again allowed to warm to room temperature and was stirred for 1 week. The mixture was then filtered in an atmosphere of dry nitrogen. The solid was identified as trimethylamine hydrochloride by comparison to an authentic sample and represented an 86% yield based on hexamethyldisilazane. The solvent was removed leaving some chlorobis(dimethylamino)borane (identity confirmed by the boiling point and by the ir spectrum) and the desired product, bis(trimethylsilyl)aminochlorodimethylaminoborane (8.9 g, 0.036 mol, 16% based on dichlorodimethylaminoborane). The product was redistilled, bp 58–59° (2.0 mm), mp −36°, density 0.91 g/ml (*ca.* 26°), $n^{26}D$ 1.4474.

Anal. Calcd for $C_8H_{24}BN_2Si_2Cl$: C, 38.32; H, 9.65; B, 4.31; N, 11.17; Si, 22.40; Cl, 14.14; mol wt 250. Found: C, 38.37; H, 10.21; B, 4.25; N, 11.20; Si, 22.53; Cl, 14.51; mol wt 250 (mass spectrum). The pmr spectrum of a neat sample gave NCH_3 (doublet; 161, 163 Hz):$SiCH_3$ (1 Hz) = 42.5:127 = 1:3 (calcd: 6:18 = 1:3) and the ^{11}B nmr spectrum gave a peak at −996 Hz.

B. Employing the experimental procedure used in A, a sample of the dichlorodimethylaminoborane dimer weighing 27 g (0.21 mol) was melted and distilled into the reaction flask. Then 0.8 molar equiv of trimethylamine (10 g, 0.17 mol) was allowed to react followed by 0.9 molar equiv of hexamethyldisilazane (31 g, 0.19 mol). After filtering out the solid trimethylamine hydrochloride and removing the solvent, 5.1 g of product I was distilled (0.020 mol, 9.5% based on dichlorodimethylaminoborane). In addition to I, however, bis(trimethylsilyl)aminobis(dimethylamino)borane (II) was found and identified by comparison of the infrared and pmr spectra to spectra of an authentic sample. Additional preparations resulted in contamination of the product by II and chlorobis(dimethylamino)borane.

Preparation of Bis(trimethylsilyl)aminobis(dimethylamino)borane (II).—The lithium salt of hexamethyldisilazane was prepared in hexane by the method given in ref 4. Thus, 0.50 mol of butyllithium (0.31 l., 1.6 *M*) was slowly added to 81 g (0.50 mol) of hexamethyldisilazane in 100 ml of dry hexane with stirring. After the evolution of butane had ceased, the solution was slowly added to a stirred mixture of 67 g (0.50 mol) of chlorobis(dimethylamino)borane in 200 ml of dry hexane. After the addition was complete, the mixture was refluxed for 3 hr. The cooled mixture was then filtered and the solvent was removed from the filtrate. The product was distilled (at 2.0 mm) until solid formed in the condenser. The receiver was then changed and the distillation was completed by heating with an infrared lamp all of the distillation apparatus except the receiver. The waxy solid product II weighed 97 g (0.38 mol, 76% yield).

Anal. Calcd for $C_{10}H_{30}BN_3Si_2$: C, 46.30; H, 11.66; B, 4.17; N, 16.20; Si, 21.66; mol wt 259. Found: C, 45.22, 45.50; H, 11.51, 11.36; B, 4.30; N, 15.44, 15.61; Si, 23.26, 21.97; mol wt 259 (mass spectrum). The pmr spectrum of a neat sample gave NCH_3 (144.5 Hz):$SiCH_3$ (−6 Hz) = 48:72 = 2:3 (calcd: 12:18 = 2:3).

Preparation of Bis(trimethylsilyl)aminochlorodimethylaminoborane (I) by Hydrogen Chloride Cleavage of Bis(trimethylsilyl)aminobis(dimethylamino)borane (II).—In a typical preparation, 37 g (0.14 mol) of II was dissolved in 500 ml of dry toluene in a 1-l. flask. The flask was attached to a vacuum manifold, cooled to −78°, and evacuated. Two equivalents (0.28 mol) of hydrogen chloride gas was measured out in a bulb of known volume and slowly added, with stirring, to the solution of II. After the addition was complete, the flask was warmed to room temperature and the solid was filtered out. The solid was identified by its infrared spectrum as dimethylamine hydrochloride. The 12 g represented 102% of the theoretical yield. The solvent was removed from the filtrate to yield 26 g of distillable material. The integration of the pmr spectrum revealed that approximately 11% of the product was II, the remaining 23 g being I (0.93 mol, 65% yield). Purification was then accomplished by careful distillation through a Nester-Faust annular Teflon spinning-band column. The infrared, pmr, and mass spectra of the purified product I were identical with the spectra of I which was prepared by the dehydrohalogenation reaction.

Determination of the Thermal Stability of Bis(trimethylsilyl)aminochlorodimethylaminoborane (I).—A sample of I weighing 4.5 g (0.018 mol) was measured into a vessel consisting of a

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

(3) P. Geymayer and E. G. Rochow, *Monatsh. Chem.*, **97**, 437 (1966).

(4) E. H. Amonoo-Neizer, R. A. Shaw, D. O. Skovlin, and B. C. Smith, *Inorg. Syn.*, **7**, 19 (1966).

(5) H Nöth and P. Fritz, *Z. Anorg. Allg. Chem.*, **322**, 297 (1963).

(6) K. Niedenzu and J. W. Dawson, *Inorg. Syn.*, **10**, 135 (1967).

(7) K. Niedenzu and J. W. Dawson, "Boron-Nitrogen Compounds," Springer-Verlag, Berlin, 1965, p 61.

(8) C. A. Brown and R. C. Osthoff, *J. Amer. Chem. Soc.*, **74**, 2340 (1952).

(9) Reference 7, p 70.

(10) A. J. Banister, N. N. Greenwood, B. P. Straughan, and J. Walker, *J. Amer. Chem. Soc.*, **86**, 995 (1964).

condenser and ground-glass joint fused onto a 50-ml flask. The vessel was attached to a vacuum line and evacuated while the sample was alternately cooled to −78° and warmed to room temperature to remove dissolved gases. A −78° trap was maintained in the system to trap out any volatile products. The pressure was then raised with dry nitrogen to approximately 510 mm and heating of the flask was initiated. Over a period of 9 days the temperature of the oil bath was raised to 235° and the pressure increased to 575 mm. During the last 24 hr of the test, compound I refluxed (bp (extrapolated to 575 mm) 205°).

A small amount of volatile material trapped out at −78° was tentatively identified as hexamethyldisiloxane by comparison of its gas-phase infrared spectrum with the published spectrum.[11] The mass spectrum, though weak, supported the same conclusion (calcd for $C_6H_{18}Si_2O$, 162; found, 162). The quantity of gas trapped out at −196° was too slight to identify positively. The presence of the hexamethyldisiloxane, however, suggests that it might have been hydrogen chloride from hydrolysis of trimethylchlorosilane. The mass spectrum was very weak but supported this conclusion (calcd for $H^{35}Cl$ and $H^{37}Cl$, 36 and 38; found, 36 and 38). These compounds could have resulted from hydrolysis of I or the decomposition products of I.

The material in the flask was found by the pmr and infrared spectra of the mixture to be mostly unchanged I plus II. By integration of the pmr resonances of the *N*-methyl protons of I and II, the mixture was found to contain approximately 4% II.

Results

After qualitative experiments indicated that, in the dehydrohalogenation reaction, less than the stoichiometric amount of trimethylamine resulted in an increased yield of the desired product, a series of 13 semiquantitative experiments such as the two given above was performed to define more closely the optimum conditions.

It was found, however, that changes in the relative proportions of the reactants altered the nature of the by-products as well as the product yield. The nature of the by-products, in turn, was found to have a profound effect on the difficulty in purifying the product. Thus, only trends could be gleaned from the experimental data. In particular, the yield of the desired product I would decrease as the mole per cent of trimethylamine decreased below or increased above about 75. Further, if the ratio of the number of moles of trimethylamine to the number of moles of hexamethyldisilazane was less than 1, the favored by-product would be bis(trimethylsilyl)aminobis(dimethylamino)borane (II) whereas a ratio greater than 1 would favor the by-product chlorobis(dimethylamino)borane. The by-product II, which will be the subject of a separate communication, is a waxy solid which sublimes as the product I distils and both contaminates the product and plugs the condenser preventing further distillation.

It was found that the waxy solid II could be prepared in high yield by direct synthesis and could then be used to prepare I *via* a hydrogen chloride cleavage reaction.[5] When a stoichiometric amount of hydrogen chloride was used, net yields of I as high as 65% were observed but the product was still contaminated by over 10% of II. Increasing the hydrogen chloride used to a 50% excess over the stoichiometric amount decreased the amount of II to approximately 5% of the distillable product but also decreased the net yield of I to about 50%. Further increases in the amount of hydrogen chloride employed to a 100% excess eliminated the contaminant II in the product but dropped the yield of I to approximately 15%. Consistent with the results found by Geymeyar and Rochow[3] for the congeners of I mentioned earlier, it was found that the compound possessed significant thermal stability. Surprisingly, however, the decomposition that did occur did not result in the formation of a borazine as was the case with bis(trimethylsilyl)aminodichloroborane.[12] Instead, after the pure compound I was exposed to temperatures in excess of 200° for 24 hr, the only decomposition product containing boron was approximately 4% II.

Discussion

The mechanism of the dehydrohalogenation reaction is not thoroughly understood, but, as Nöth stated, "...if the Lewis acidity of the boron halide and the Lewis basicity of the amine decrease, the 1:1 complex may not form at all or only in an extremely small concentration."[13] Thus, the decreased acidity of dichlorodimethylaminoborane (compared to trichloroborane) and the relatively low basicity of silicon-substituted amines such as hexamethyldisilazane[14] would indicate a reaction mechanism other than one involving formation of an adduct with hexamethyldisilazane. If the mechanism involves the protonolysis of a boron–chlorine bond,[15] hydrogen chloride could be released which could cleave a dimethylamino group from dichlorodimethylaminoborane or its trimethylamine adduct (or derivatives thereof) as a reaction competing with the formation of trimethylamine hydrochloride. The dimethylamine produced could then react with dichlorodimethylaminoborane to produce chlorobis(dimethylamino)borane or react with I to form II, thus explaining the presence of the two observed by-products.

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[15] G. Urry in "The Chemistry of Boron and Its Compounds," E. L. Muetterties, Ed., Wiley, New York, N. Y., 1967, p 331.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ARIZONA, TUCSON, ARIZONA 85721

A Study of the Reaction of Sodium Dimethylamidotrihydroborate(1−) with Diborane

BY PHILIP C. KELLER

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We recently reported a new synthesis of μ-$(CH_3)_2NB_2H_5$ based on the reaction of $Na(CH_3)_2NBH_3 \cdot 0.5C_4H_8O_2$ with diborane (eq 1).[1] Examination of this

$$Na(CH_3)_2NBH_3 + B_2H_6 \longrightarrow \mu\text{-}(CH_3)_2NB_2H_5 + NaBH_4 \quad (1)$$

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[1] P. C. Keller, *J. Amer. Chem. Soc.*, **91**, 1231 (1969).