VI_2 and VI_3 was suspected. Subsequently a series of equilibration reactions between VI_2 and excess liquid I_2 was performed at various temperatures for times of 5–30 days. The solid products resulting from reactions at 196, 215, and 238° were found to have I:V ratios of 2.33, 2.55, and 2.61, respectively. Thus solid solution formation seemed to be confirmed.

However, when these products were thoroughly ground to pass completely through a 200 mesh screen, lines of VI_2[5] were clearly evident in the X-ray powder patterns along with the original lines noted above. The latter set of lines was subsequently found to match the pattern of pure VI_3, which proved that the "equilibration" reactions had produced only mixtures and not solid solutions. It is quite remarkable that complete conversion of VI_2 to VI_3 in such reactions is not attained after several weeks, even at temperatures up to 273°. Apparently a layer of VI_3 is formed on the crystals of VI_2, and this impedes or nearly halts further conversion to VI_3.

Successful preparation of pure VI_3 may be effected as noted in the Experimental Section. To facilitate the reaction the V metal should be kept at a temperature greater than *ca.* 500° and I_2 should be at 240–300°. Precautions should be taken to prevent damage to equipment or injury to personnel in the event of explosion of the reaction tubes, since the tubes must contain *ca.* 5–10 atm of I_2.

The black micaceous crystals of VI_3 were found to have the hexagonal BiI_3 structure. After assigning indices to all lines in the powder pattern the following lattice constants were obtained from the refinement calculations: $a = 6.919 \pm 0.002$ Å, $c = 19.91 \pm 0.01$ Å, $c/a = 2.876$. The observed and calculated d spacings are given in Table III.

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Isolation and Characterization of Diborazinylamine[1]

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The reactions of B-monoaminoborazine with diborane, BF_3, and HBr have been investigated. A slightly volatile product sublimed from the reaction products has been identified mass spectrometrically as $B_6N_7H_{11}$. Evidence from mass, infrared, and boron-11 nmr spectra indicate the compound is diborazinylamine.

Introduction

In the large number of publications in borazine chemistry relatively little work has been reported on the reactions of B-monosubstituted borazine derivatives. Only quite recently have experimental studies with B-monochloroborazine been published.[2] We recently described a photochemical procedure for the preparation of B-monoaminoborazine[3] in quantities adequate for chemical study. Since this compound contains a terminal amino group, it was anticipated that new derivatives could be obtained by its reactions with Lewis acids. In this paper, results of a series of studies of the reactions of aminoborazine with B_2H_6, BF_3, and HBr are discussed.

Experimental Section

Samples of B-monoaminoborazine were prepared by the photolysis of borazine–ammonia mixtures.[3] Aminoborazine was identified by its infrared spectrum.[3] Some experiments were conducted with amino(^{15}N)borazine which was prepared from $^{15}NH_3$ and borazine with the natural isotopic composition. Most experiments were performed with samples weighing between 50 and 20 mg. The reactants were mixed by adding the acid, initially in the gas phase, to the liquid aminoborazine and then freezing the mixture to −196°. The reaction vessel was then warmed to room temperature and the reaction was allowed to proceed for several hours. The unreacted acid was then removed. For quantitative stoichiometry measurements the samples of aminoborazine were weighed in a Pyrex tube containing a break-seal, and the quantity of acid added was determined from initial and final pressure measurements. The borazine used was prepared from NH_4Cl and $LiBH_4$[4] and purified by the addition of ammonia[3] to remove aminodiborane.

B-Monoaminoborazine–B_2H_6 Reaction.—Reaction between aminoborazine and B_2H_6 produced a white polymeric substance that evolved hydrogen at room temperature. After the evolution of hydrogen ceased, the residue was sublimed *in vacuo* at 25° for several hours and a slightly volatile substance was collected in a small Pyrex bulb held at −13° in a glycol slush bath. When this material was resublimed at 50°, needlelike crystals condensed on the cooler walls of the vessel. A mass spectrum of this material is given in Table I. Similar experiments starting with amino(^{15}N)borazine yielded a substance whose mass spectrum is also given in Table I. The infrared spectrum of a solid film of the

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(1) Work supported by the Army Research Office (Durham) and the Advanced Research Projects Agency.

(2) R. Maruca, O. T. Beachley, Jr., and A. W. Laubengayer, *Inorg. Chem.*, **6**, 575 (1967).

(3) G. H. Lee, II and R. F. Porter, *ibid.*, **6**, 648 (1967).

(4) G. W. Schaeffer, R. Schaeffer, and H. J. Schlesinger, *J. Am. Chem. Soc.*, **73**, 1612 (1951).

TABLE I

MASS SPECTRA OF PRODUCTS IN THE REACTIONS OF B-MONOAMINOBORAZINE AND B_2H_6 (COLUMNS 1–3; 7–9) AND B-MONOAMINO(^{15}N)BORAZINE AND B_2H_6 (COLUMNS 5 AND 6; 11 AND 12) (ELECTRON ENERGY 75 V, INTENSITIES RELATIVE TO MOST INTENSE PEAK 100.0)

m/e	Intens	Major ion[a]	Comments	*m/e*	Intens
50	3.9			50	3.6
51	29.8			51	25.3
52	89.6			52	98.0
53	100.0	$B_2N_2H_3^+$	Prominent peak in borazine[b]	53	100.0
				54	20.4
61	2.6			61	2.4
62	6.5			62	7.2
63	7.8	$B_3N_2H_2^+$	Appears in borazine spectrum	63	8.4
65	1.3			65	1.2
66	5.2			66	4.7
67	22			67	21.7
68	23.3	$B_2N_3H_4^+$	Prominent in aminoborazine[c]	68	31.3
				69	16.8
75	3.9			75	3.6
76	16.8			76	13.2
77	42.8			77	31.3
78	45.4	$B_3N_3H_3^+$	Prominent in monosubstituted borazine derivatives[c,d]	78	40.9
79	10.4			79	25.3
80	11.7	$B_3N_3H_5^+$	Prominent peaks in borazine	80	20.5
81	1.3	$B_3N_3H_6^+$		81	6.0
91	11.7			91	4.7
92	25.9			92	14.4
93	29.8	$B_3N_4H_4^+$		93	24.0
94	9.0			94	20.4
95	10.4	$B_3N_4H_6^+$	Prominent in aminoborazine	95	16.8
96	3.9	$B_3N_4H_7^+$		96	20.4
				97	10.8
99	1.3			99	0.0
100	3.9			100	1.2
101	7.8			101	3.6
102	12.9			102	8.4
103	11.7	$B_4N_4H_3^+$		103	10.8
				104	6.0
115	1.3			115	0.0
116	2.6			116	1.2
117	6.5			117	3.6
118	7.8	$B_4N_5H_4^+$		118	6.0
				119	6.0
124	2.6			124	1.2
125	1.3			125	1.2
126	2.6			126	1.2
127	3.9			127	2.4
128	3.9			128	3.6
129	2.6			129	3.6
130	2.6			130	2.4
131	1.3			131	1.2
132	1.3	$B_5N_5H_7^+$	Corresponds to $B_2NH_2^+$ in borazine (loss of neutral species of composition BN_2H_4)	132	1.2
142	1.3			142	1.2
143	2.6			143	1.2
144	3.9			144	2.4
145	5.2			145	3.6
146	5.2			146	4.7
147	5.2	$B_5N_6H_8^+$	Corresponds to $B_2N_2H_3^+$ in borazine (loss of neutral species of composition BNH_3)	147	4.7
				148	3.6
153	2.6			153	1.2
154	5.2			154	2.4
155	10.4			155	6.0
156	15.6			156	10.8
157	9.1	$B_6N_6H_7^+$	Corresponds to $B_3N_2H_2^+$ in borazine (loss of neutral species of composition NH_4)	157	12.0
				158	7.2
168	5.2			168	2.4
169	11.7			169	6.0
170	23.4			170	13.2
171	37.6			171	26.4
172	53.2			172	39.6
173	74.0			173	56.6
174	93.5			174	74.7
175	57.1	$B_6N_7H_{11}^+$	Parent	175	81.9
176	3.9			176	40.9
				177	1.2

[a] Only principal ions are indicated; a complete breakdown of each mass grouping into fragments due to loss of H atoms is not shown. [b] Mass spectral data from American Petroleum Institute Project 44, Serial No. 1346, July 31, 1956. [c] G. H. Lee, II, and R. F. Porter, *Inorg. Chem.*, **6**, 648 (1967). [d] M. Nadler and R. F. Porter, *ibid.*, **6**, 1739 (1967).

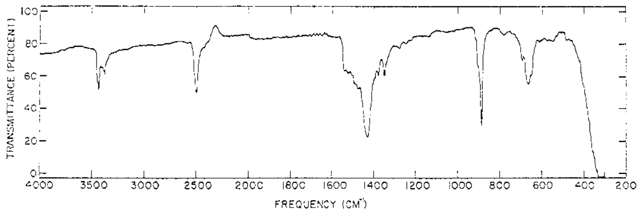

Figure 1.—Infrared spectrum of solid film of $B_6N_7H_{11}$.

product deposited on a liquid nitrogen cooled KBr window is shown in Figure 1. The spectrum was obtained on a Perkin-Elmer Model 521 grating spectrophotometer. In a typical experiment it was found that 0.623 mmol of aminoborazine reacted with 0.182 mmol of B_2H_6 to yield 25.2 mg of separated product. The molar ratio of B_2H_6 to aminoborazine reacting is thus about 3.4. Elemental analysis of the product was consistent with a compound of empirical formula $B_6N_7H_{11}$. *Anal.* Calcd for $B_6N_7H_{11}$: B, 37.7; N, 56.0; H, 6.3. Found: B, 37.93; N, 55.53; H, 6.45. The compound melts at 34° in an atmosphere of argon and decomposes by evolving borazine if maintained at room temperature for several hours. The ^{11}B nmr spectrum of the sublimed product dissolved in triethylamine was obtained on a Varian HA-60 spectrometer operating at 15 MHz.[5] Little information could be obtained from hydrogen nmr of the compound since the signals were broad and poorly defined. A solid residue from the reaction continued to evolve small amounts of H_2 after the condensable product was removed. This residue was not characterized further.

B-Monoaminoborazine–HBr Reaction.—The reaction of aminoborazine with HBr yielded a white solid material which did not evolve hydrogen at room temperature. Sublimation of this substance under conditions similar to those described for the B_2H_6 reaction yielded a product having the mass spectrum identical with that shown in Table I. Under typical reaction conditions 0.170 mmol of HBr reacted with 0.351 mmol of aminoborazine to give a nominal reaction ratio of $H_3N_3B_3H_2NH_2$:HBr = 2:1. X-Ray analysis of the residue after removal of the product indicated that NH_4Br was the major constituent.[6]

B-Monoaminoborazine–BF$_3$ Reaction.—Reaction of aminoborazine with BF_3 gave a white solid which evolved on sublimation the product with the mass spectrum shown in Table I. The stoichiometry of this reaction was not checked but it was found that the best yields of product were obtained when the starting ratio of $H_3N_3B_3H_2NH_2$ to BF_3 was 2:1. The residue of the reaction under those starting conditions was found by X-ray analysis[7] to be the $NH_3 \cdot BF_3$ addition product.

Results and Discussion

Mass spectral data for the separated products of the aminoborazine–B_2H_6, –HBr, and –BF_3 reactions indicate a nominal molecular weight of 175 mass units.

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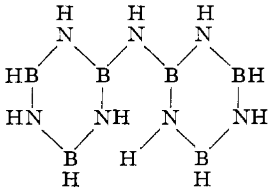
(5) The authors wish to thank Professor O. T. Beachley and Mr. D. H. Templeman for obtaining the ^{11}B nmr spectrum.

(6) ASTM Card No. 5-0618.

(7) C. W. Keenan and W. J. McDowell, *J. Am. Chem. Soc.*, **75**, 6348 (1953).

The product of reaction with amino(^{15}N)borazine is increased in mass by 1 unit, indicating that one ^{15}N atom was introduced through the amino group. Substantial ring cleavage resulting in scrambling of ^{15}N would lead to a distribution in molecular weight with some mass peaks above 176. In Table I we indicate similarities in the ion-fragmentation patterns of the product and those for borazine[8] and some monosubstituted borazine derivatives.[3,9] In a number of cases, a major ion peak in borazine has an analog in the product resulting from loss of the same neutral fragment (or fragments). From these considerations, the composition of the product is established as $B_6N_7H_{11}$. Calculations based on the natural isotope abundances of ^{15}N and deuterium (0.37 and 0.015%, respectively[10]) gave for a species $B_6N_7H_{11}$, containing one labeled ^{15}N in the preparation, a natural abundance ratio of 0.024 of mass 117 to mass 176. The experimental intensity ratio was found to be 0.029 and is in fairly good agreement with the calculated ratio. The calculated natural abundance ratio of mass 176 to mass 175 in the unlabeled product is 0.028 while the experimental intensity ratio is 0.068. A probable explanation for an abnormally high mass 176 peak in the unlabeled compound is the presence of a small quantity of diborazinyl ether[3] (highest mass 176) that is produced when traces of water vapor are present in the photochemical preparation of the aminoborazine. Referring once again to Table I it is noted that a number of the higher mass fragments of $B_6N_7H_{11}$ are 94 mass units (95 in the case of the ^{15}N-labeled compound) higher than prominent peaks in the mass spectrum of borazine. Ions of mass 157 and 147 are 94 mass units higher than the ions $B_2N_2H_3^+$ (*m/e* 53) and $B_3N_2H_2^+$ (*m/e* 63) produced in the fragmentation of borazine. This relationship suggests that $B_6N_7H_{11}$ has a structure derived by replacement of a $B_3N_4H_6$ unit, containing the amino nitrogen, for one H atom in borazine. This leads to the proposed configuration



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for diborazinylamine.

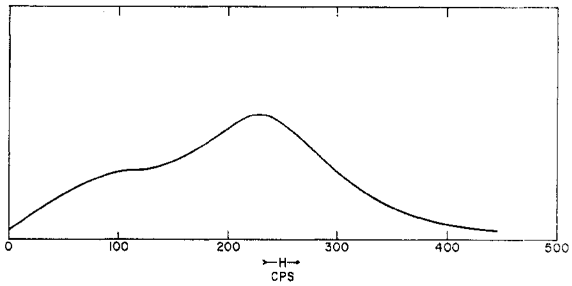

Figure 2.—Boron-11 nmr spectrum of $B_6N_7H_{11}$. The zero point is arbitrarily chosen.

The ^{11}B nmr spectrum of the aminoborazine–B_2H_6 reaction product (Figure 2) shows a broad asymmetrical doublet. This can be interpreted as the overlap of a single resonance from one type of ^{11}B not coupled to a hydrogen atom and a broad doublet (with center at slightly lower field) resulting from H–^{11}B coupling. The spectrum is consistent with structure I having two equivalent B atoms without terminal H atoms and four nearly equivalent B atoms each with one terminal hydrogen. The H–^{11}B coupling constant was estimated to be between 125 and 140 cps. The corresponding value in borazine is 136 cps.[11]

In Table II are listed infrared frequencies for a number of bands in the solid film spectrum of $B_6N_7H_{11}$ (Figure 1). The assignments given are based on interpretations of the spectra of borazine[12] and aminoborazine.[13] The strong bands at 3437, 2495, 1425, and 882 cm^{-1} are indicative of group vibrations of the borazine ring.

TABLE II

INFRARED SPECTRA OF LIQUID NITROGEN COOLED FILM OF $B_6N_7H_{11}$

Freq, cm^{-1}	Intens[a]	Probable assignment
3437	s	N–H (ring) str
3378	m	N–H (amino) str
2498	s	B–H stretch
1530	m, b	N–H (amino) bend
1485	m, b	B–N (amino) str
1425	vs	B–N (ring) str
1376	m	
1350	m	B–N (ring) str
1275	w	B–N (amino) str
1245	w	
1220	w	
882	vs	B–H bend (normal to ring)
780	w	
690	m	
660	s	(B–N (ring bend) (normal to ring)
645	sh	
540	w	

[a] Abbreviations: s, strong; m, medium; w, weak; v, very; b, broad, sh, shoulder.

Of the reactions used above to prepare $B_6N_7H_{11}$, the aminoborazine–HBr system appears to be the simplest to interpret in terms of stoichiometry. From the observations that about 0.485 mol of HBr reacts per mole of aminoborazine and that there is NH_4Br in the product residue, we can visualize the ideal stoichiometry: $2H_3N_3B_3H_2NH_2 + HBr \rightarrow B_6N_7H_{11} + NH_4Br$.

In the aminoborazine–diborane reaction approximately 3.4 mol of $H_3N_3B_3H_2NH_2$ was required per mole

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[8] Mass spectral data from American Petroleum Institute Research Project 44, Serial No. 1346, July 31, 1956.

[9] M. Nadler and R. F. Porter, *Inorg. Chem.*, **6**, 1739 (1967).

[10] "Handbook of Chemistry and Physics," 49th ed, The Chemical Rubber Publishing Co., Cleveland, Ohio, 1968, pp B-6 and B-7.

[11] W. D. Phillips, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **81**, 4496 (1959).

[12] K. Niedenzu, W. Sawodny, H. Watanabe, J. W. Dawson, T. Totani, and W. Weber, *Inorg. Chem.*, **6**, 1453 (1967).

[13] R. F. Porter and E. S. Yeung, *ibid.*, **7**, 1306 (1968).

of B_2H_6 reacting. If we assume that the solid residue of this reaction is initially an ammonia–borane addition compound, then we can write for the idealized stoichiometry

$$B_2H_6 + 4H_3N_3B_3H_2NH_2 \longrightarrow 2B_6N_7H_{11} + \text{addition product} \longrightarrow xH_2 + \text{polymeric substance}$$

The formation of the $NH_3 \cdot BF_3$ addition compound in the reaction with BF_3 complements evidence from the other reactions that a common feature is the elimination of ammonia from two molecules of aminoborazine to form a stable salt with the acid. These results are perhaps not surprising when considered in relation to the analogous aniline–HCl reaction which yields diphenylamine and NH_4Cl.[14]

(14) A. Contardi, *Giorn. Chim. Appl.*, **1**, 11 (1920).

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Synthesis and Properties of Some Bis(ligand)dihydroboron(n+) Salts[1]

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Salts containing bis(ligand)dihydroboron(1+) ions of the type $LL'BH_2^+$, where L and L′ are electron-donating ligands coordinated to boron through different group V or VI elements, including nitrogen, phosphorus, arsenic, and sulfur, have been prepared by displacement of halide ion from a (trialkyl donor)–haloborane adduct by the appropriate neutral ligand. Halide and hexafluorophosphate salts of the compounds have been characterized. The method is quite general for the preparation of a wide variety of boronium ions, as further illustrated by the synthesis of chelated boron(1+) ions and a dinuclear boron(2+) ion from the reaction of N,N,N′,N′-tetramethylethylenediamine with mono- and dihaloborane adducts of trimethylamine.

Introduction

Since Parry and coworkers showed the diammoniate of diborane to be the tetrahydroborate salt of the diamminedihydroboron(1+) ion,[3] numerous examples of the synthesis and characterization of salts containing four-coordinate boron cations have been reported.[4–10] Although most of these have been of the type $L_2BH_2^+$, in which two identical neutral electron donor ligands are coordinated to boron, a few examples of preparations of ions containing two different boron-bonded tertiary amines have been described.[7b,9e] The synthetic method of Nöth and Beyer,[4] involving displacement of halide from a haloamine–borane, has been found to be convenient for the preparation of both types of bis(amine)-boronium salts.

We wish to relate the use of a modification of this synthesis for the preparation of a wide variety of four-coordinate boronium ions including those in which the boron atom is coordinated to two different kinds of neutral ligands wherein one (or both) of the ligands is something other than a nitrogen base. Some specific examples of the synthesis of such ions containing boron bonded to tertiary phosphines, arsines, and dimethyl sulfide as well as tertiary amines are described.[1] In each case, the reaction can be regarded as a nucleophilic displacement of halide ion from a donor–haloborane adduct by a second donor (the entering nucleophile). The study of the scope of this type of substitution has been extended to the use of N,N,N′,N′-tetramethylethylenediamine as a nucleophile in the synthesis of chelated boron(1+) ions and a dinuclear divalent boron(2+) ion.[11]

Experimental Section

Where analytical data are not provided with a preparative procedure for a salt, the composition of the cation is confirmed by analysis of the hexafluorophosphate salt reported in Table I.

Materials.—Trimethylamine–borane was obtained from Matheson Coleman and Bell and purified by sublimation *in vacuo*. Triethylphosphine (Strem Chemicals) was used without further purification. Trimethylamine–haloboranes were synthesized by methods similar to those of Nöth and Beyer[4] by allowing tri-

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(1) Presented in part at the 156th National Meeting, American Chemical Society, Atlantic City, N. J., Sept 13, 1968; see Abstracts, No. INOR 162.

(2) NDEA Research Fellow, 1966–1969.

(3) (a) S. G. Shore and R. W. Parry, *J. Am. Chem. Soc.*, **77**, 6084 (1955); (b) D. R. Schultz and R. W. Parry, *ibid.*, **80**, 4 (1958); (c) S. G. Shore and R. W. Parry, *ibid.*, **80**, 8, 12 (1958); (d) R. W. Parry and S. G. Shore, *ibid.*, **80**, 15 (1958); (e) S. G. Shore, P. R. Girardot, and R. W. Parry, *ibid.*, **80**, 20 (1958); (f) R. W. Parry, G. Kodama, and D. R. Schultz, *ibid.*, **80**, 24 (1958); (g) R. C. Taylor, D. R. Schultz, and A. R. Emery, *ibid.*, **80**, 27 (1958).

(4) (a) H. Nöth, *Angew. Chem.*, **72**, 638 (1960); (b) H. Nöth and H. Beyer, *Ber.*, **93**, 2251 (1960); (c) H. Nöth, H. Beyer, and H.-J. Vetter, *ibid.*, **97**, 110 (1964).

(5) J. E. Douglass, *J. Am. Chem. Soc.*, **86**, 5431 (1964).

(6) (a) S. G. Shore and K. W. Boddeker, *Inorg. Chem.*, **3**, 914 (1964); (b) S. G. Shore, C. W. Hickam, Jr., and D. Cowles, *J. Am. Chem. Soc.*, **87**, 2755 (1965).

(7) (a) H. C. Miller, N. E. Miller, and E. L. Muetterties, *ibid.*, **85**, 3885 (1963); (b) N. E. Miller and E. L. Muetterties, *ibid.*, **86**, 1033 (1964); (c) E. L. Muetterties, *Pure Appl. Chem.*, **10**, 53 (1965).

(8) P. C. Moews, Jr., and R. W. Parry, *Inorg. Chem.*, **5**, 1552 (1966).

(9) (a) G. E. Ryschkewitsch, *J. Am. Chem. Soc.*, **89**, 3145 (1967); (b) G. E. Ryschkewitsch and J. M. Garrett, *ibid.*, **89**, 4240 (1967); **90**, 7234 (1968); (c) C. W. Makowsky, G. L. Galloway, and G. E. Ryschkewitsch, *Inorg. Chem.*, **6**, 1972 (1967); (d) K. C. Nainan and G. E. Ryschkewitsch, *ibid.*, **7**, 1316 (1968); (e) K. C. Nainan and G. E. Ryschkewitsch, *J. Am. Chem. Soc.*, **91**, 330 (1969).

(10) M. Inoue and G. Kodama, *Inorg. Chem.*, **7**, 430 (1968).

(11) The preparation of this dinuclear ion by another method as well as the synthesis of other unsymmetrical boron(1+) and (2+) ions by similar displacement reactions has been recently reported: N. E. Miller, D. L. Reznicek, R. J. Rowatt, and K. R. Lundberg, *ibid.*, **8**, 862 (1969).