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Boron-11 Nuclear Magnetic Resonance Study of the 7,9-$B_9C_2H_{12}^-$ Ion and Some Substituted Derivatives

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The 70.6-MHz ^{11}B NMR spectrum of 7,9-$B_9C_2H_{12}^-$ consists of six doublets of relative intensities 2:1:2:2:1:1 reading upfield which are assigned to B(2,5), B(8), B(3,4), B(10,11), B(6), and B(1), respectively. Substituted 7,9-$B_9C_2H_{12}^-$ derivatives obtained by reaction of Lewis bases [e.g., $CH(CN)_2^-$, $OC_2H_5^-$, and $N(C_2H_5)_3$] with *closo*-2,3-$B_9H_9C_2R_2$ (R = H, CH_3) have the base attached at B(10).

Introduction

The application of ^{11}B NMR spectral information to boron hydride research has been in existence for almost as long as the use of proton NMR spectral data in organic chemistry. However, the utilization of ^{11}B NMR data has lagged far behind proton NMR applications. This shortcoming in boron NMR has been due to (a) poor spectral resolution, (b) insufficient understanding of the relationships of ^{11}B chemical shifts to molecular structure, and (c) inadequate understanding of the bonding in boron hydrides, particularly the higher boron hydrides. With the advent of high-field Fourier transform NMR instruments and associated techniques, the resolution problem is rapidly being overcome. It is now of importance to determine the specific assignment of each boron resonance to a particular boron atom in a molecule and to do these studies for a large number of classes of boron hydride molecules. In this manner generalized empirical rules concerning structure–chemical shift relationships will be found. Such rules will greatly enhance the usefulness of ^{11}B NMR measurements.

Recently we and others have carried out structure–chemical shift studies of $B_{10}H_{12}(\text{ligand})_2$,[2] $B_9H_{13}(\text{ligand})$,[3] $B_{10}H_{13}^-$,[4] $B_9H_{12}S^-$,[5] and 7,8-$B_9C_2H_{12}^-$.[6-8] In this paper we outline our study of the ^{11}B NMR spectra of 7,9-$B_9C_2H_{12}^-$ and specifically substituted derivatives by which we have elucidated the majority of the boron atom–chemical shift relationships of this carborane anion.

Experimental Section

The ^{11}B NMR spectra were measured on equipment consisting of a pulsed NMR apparatus built in this department operating at 70.6 MHz, a Varian 51.7-kg superconducting magnet, and a 16K Nicolet 1080 series computer. Additional details have been reported elsewhere.[9] The ^{11}B NMR spectra were externally referenced to $BF_3{\cdot}O(C_2H_5)_2$.

Spin–lattice relaxation measurements were made by the inversion–recovery method[10] at 70.6 MHz using a 40-μsec 180° pulse and a recycle time of 610 msec. Probe temperature was maintained at 26 ± 1° for all T_1 measurements.

One thousand twenty-four scans were accumulated with a sweep width of 5000 Hz at each of 16 τ values in the range of 300–22 msec (inclusive). Spin–lattice relaxation times were determined by a linear least-squares fit of the data to the equation

$$T_1 = \frac{N\Sigma\tau_i^{\,2} - (\Sigma\tau_i)^2}{N(\Sigma L_i\tau_i) - (\Sigma L_i\Sigma\tau_i)}$$

where $L_i = \ln(1 - A_i/A_\infty)$, A_i is the peak amplitude at τ_i, and N is the number of τ's observed [$|A_\tau| \geq |A_\infty - 0.05A_\infty|$ values are omitted in the calculation of T_1]. We feel the accuracy of the T_1 values calculated by this method is better than ±10% and the standard deviation for the least-squares fit is better than ±3% of T_1 for all peaks.

The method of Hawthorne[11] was used to convert 1,7-$B_{10}C_2H_{12}$ and 9,10-Br_2-1,7-$B_{10}C_2H_{10}$ to 7,9-$B_9C_2H_{12}^-$ and 1,6-Br_2-7,9-$B_9C_2H_{10}^-$, respectively. Anal. Calcd for $(CH_3)_4N[B_9C_2H_{10}Br_2]$: C, 19.72; H, 6.06; Br, 43.74. Found: C, 20.00; H, 6.43; Br, 44.04. The synthesis of Cs[3,4-$O_2C_6H_4$-7,9-$(CH_3)_2$-7,9-$B_9C_2H_8$] (where $O_2C_6H_4$ is 1,2-phenylenedioxy) has been reported elsewhere.[12]

$(CH)_4N[C_2H_5OB_9C_2H_{11}]$. To 0.47 g (3.54 mmol) of 2,3-$B_9C_2H_{11}$ was added a solution containing 39.2 g (0.7 mol) of KOH in 40 ml of ethanol. The solution was stirred for 15 min and then CO_2 was bubbled through the solution to precipitate the excess KOH as K_2CO_3. The mixture was filtered and 20 ml of saturated aqueous tetramethylammonium chloride solution was added to the filtrate. The volume of reaction mixture was reduced to approximately 20 ml on a rotary evaporator. The resulting white crystalline product was collected and recrystallized from acetone–water. The quantity of $(CH_3)_4N[C_2H_5OB_9C_2H_{11}]$ obtained was 0.48 g (54% yield). Anal. Calcd for $C_8H_{28}B_9NO$: C, 38.17; H, 11.22. Found: C, 37.56; H, 10.82. This compound decomposes in the solid state at a moderate rate upon exposure to the atmosphere. The compound was stored in an evacuated vial prior to obtaining its elemental analysis.

$(C_2H_5)_3N{\cdot}B_9H_9C_2(CH_3)_2$. In a 100-ml, three-neck flask equipped with a magnetic stirring bar, gas inlet, and addition funnel was dissolved 2,3-dimethyl-2,3-dicarba-*closo*-undecaborane(11) (0.1 g, 0.62 mmol) in 20 ml of freshly distilled benzene. The triethylamine (0.3 g, 3.0 mmol) was dissolved in 10 ml of freshly distilled benzene in the addition funnel and this solution was added dropwise to the stirred solution in the flask over a 5-min period. The resulting solution was allowed to stir an additional 15 min after completing the addition. The benzene and excess triethylamine were removed at low pressure and the white residue was dried under vacuum. The product was recrystallized from acetonitrile to give 0.07 g (51%, 0.3 mmol) of the adduct. Anal. Calcd for $C_{10}H_{30}B_9N$: C, 45.88; H, 11.56; N, 5.35. Found: C, 45.96; H, 11.44; N, 5.04.

Results and Discussion

The 70.6-MHz ^{11}B NMR spectrum of $(CH_3)_3NH$[7,9-$B_9C_2H_{12}$] is presented in Figure 1. The numbering system of the nido anion is given on the right-hand side of Figure 2. The boron NMR spectrum of the bridge-deuterated derivative was previously described[7] and this indicated that the resonance centered at 22.3 ppm was associated with atoms B(10) and B(11). These atoms are located on the open face of the anion and share a single bridge hydrogen atom. This result was confirmed by observing the ^{11}B NMR spectrum while proton decoupling the bridge hydrogen resonance which yielded two

Table I. ^{11}B NMR Data for Some 7,9-$B_9C_2H_{12}^-$ Derivatives

Compd	Feature	Chem shift, ppm (J, Hz)	Rel area
$(CH_3)_4N\{10\text{-}[CH(CN)_2]\text{-}7,9\text{-}B_9C_2H_{11}\}$[a]	Doublet	+2.0[b]	1
	Doublet	+3.9[b]	1
	Doublet	+5.4[b]	1
	Doublet	+13.6 (51)	1
	Doublet	+20.5[b]	1
	Doublet	+22.7[b]	2
	Doublet	+33.8[b]	2
$(CH_3)_4N[3,4\text{-}O_2C_6H_4\text{-}7,9\text{-}(CH_3)_2\text{-}7,9\text{-}B_9C_2H_8]$[c]	Doublet	−0.5 (134)	1
	Singlet	+3.3	2
	Doublet	+5.5 (151)	2
	Doublet of doublets	+25.6 (134, 46)	2
	Doublet	+31.6 (139)	1
	Doublet	+41.4 (142)	1
$(CH_3)_4N[1,6\text{-}Br_2\text{-}7,9\text{-}B_9C_2H_{10}]$	Doublet	+1.9 (150)	2
	Doublet	+4.6 (145)	1
	Singlet	+20.1	6
	Multiplet	+18–22 region	
$10\text{-}[N(C_2H_5)_3]\text{-}7,9\text{-}B_9C_2(CH_3)_2H_9$	Doublet	0.0 (137)	1
	Doublet	+1.9[b]	1
	Doublet	+3.7[b]	1
	Doublet	+9.7 (48)	1
	Doublet	+14.6 (154)	1
	Doublet	+18.7 (151)	1
	Doublet of doublets	+21.5 (139, 43)	1
	Doublet	+33.9[b]	1
	Doublet	+34.5[b]	1

[a] Acetone solvent. [b] This signal was overlapped with another signal so that an accurate coupling constant could not be obtained. [c] $O_2C_6H_4$ = 1,2-phenylenedioxy.

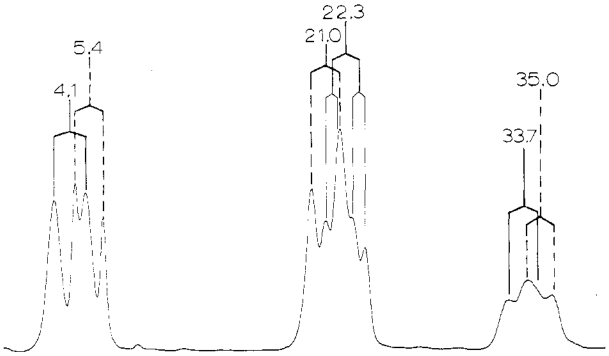

Figure 1. The 70.6-MHz ^{11}B NMR spectrum of $(CH_3)_3NH[7,9\text{-}B_9C_2H_{12}]$ in acetonitrile solution.

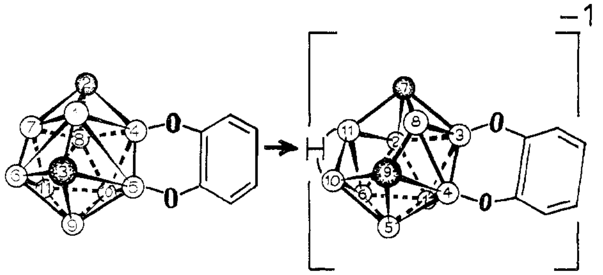

Figure 2. Proposed opening of 2,3-$(CH_3)_2$-2,3-$B_9C_2H_9(O_2C_6H_4)$ to form $[3,4\text{-}O_2C_6H_4\text{-}7,9\text{-}(CH_3)_2\text{-}7,9\text{-}B_9C_2H_8]^-$. The methyl groups have been left off the carbon atoms for clarity.

sharp overlapping doublet signals of equal intensity. The structure of 9,10-Br_2-1,7-$B_{10}C_2H_{10}$ was determined previously by a single-crystal X-ray diffraction study.[13] Base degradation of this dibromo derivative is assumed to proceed in the normal manner to form the $[1,6\text{-}Br_2\text{-}7,9\text{-}B_9C_2H_{10}]^-$ ion. The ^{11}B NMR data for this derivative are given in Table I. The two resonances each of unit area at 33 and 35 ppm in the spectrum of the parent ion are found as a large singlet at 20.1 ppm in the boron NMR spectrum of the dibromo derivative. Previous observations suggest that substitution of bromine for hydrogen will cause a polyhedral boron resonance to be found at lower field. This suggests that the signals at 33 and 35 ppm in Figure 1 are due to B(1) and B(6).

Table II. Boron-11 Spin-Lattice Relaxation Times of $(CH_3)_3NH[7,9\text{-}B_9C_2H_{12}]$

Chem shift, ppm	T_1, msec	Proposed assignment	Chem shift, ppm	T_1, msec	Proposed assignment
4.1	36	B(2,5)	22.3	34	B(10,11)
5.4	44.5	B(8)	33.7	77	B(6)
21.0	43.5	B(3,4)	35.0	90	B(1)

Boron-11 spin–lattice relaxation times have been measured for $(CH_3)_3NH[7,9\text{-}B_9C_2H_{12}]$ in acetonitrile solution and are presented in Table II. We have obtained T_1 measurements on several other nido molecules, including 7,8-$B_9C_2H_{12}^-$, whose ^{11}B resonances have been assigned previously.[14] In all cases we find that the boron atom with the most symmetrical field gradient around the BH bond axis has the longest T_1 relaxation time. No anisotropy in the rotational correlation tensor has been observed in unsubstituted compounds of this nido structural type. On this basis we propose that the doublet at 35 ppm in the ^{11}B NMR spectrum of 7,9-$B_9C_2H_{12}^-$ is associated with B(1). The resonance at 34 ppm is then due to B(6), and therefore, by a process of elimination, the sharp doublet at 5.4 ppm must be due to B(8).

The closo molecule 1,8-$(CH_3C)_2B_9H_7$-3,7-$O_2C_6H_4$[12a] (where $O_2C_6H_4$ = 1,2-phenylenedioxy, here and elsewhere in this paper) can be reduced with sodium (naphthalene carrier) and subsequent hydrolysis generates the substituted nido anion $[(CH_3C)_2B_9H_8(O_2C_6H_4)]^-$.[12b] Simple cage opening of the closo derivative can occur in one of two ways. One mode of opening is illustrated in Figure 2 to give an anion product which has the $O_2C_6H_4$ group attached at B(3) and B(4). In the other mode of cage opening B(1) in the closo compound moves away from the $O_2C_6H_4$ substituent so that the resulting anion has the substituent attached at B(10) and B(11) on the open face. This is essentially the cage-opening mechanism proposed earlier by Rudolph and coworkers.[15] The ^{11}B NMR spectrum of this anion is illustrated in Figure 3. The simplicity of this spectrum

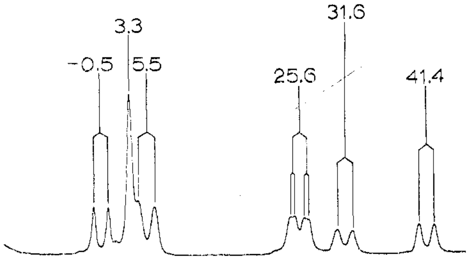

Figure 3. The 70.6-MHz ^{11}B NMR spectrum of Cs[3,4-$O_2C_6H_4$-7,9-$(CH_3)_2$-7,9-$B_9C_2H_8$] in acetone solution.

indicates that the anion is quite symmetrical and suggests that no unusual rearrangement has occurred during cage opening of the anion. The doublet of doublets signal of area 2 centered at +25.6 ppm can be attributed to the B(10,11) positions of this anion which show both terminal and bridge-hydrogen spin coupling. Therefore if the simple cage-opening process is correct, the $O_2C_6H_4$ group is substituted at B(3,4). Substitution of an OR group for H on a boron atom of a polyhedral molecule generally causes a downfield shift of that resonance.[3] On the basis of this information the doublet at 21.0 ppm in Figure 1 can be assigned to B(3,4). The only doublet of area 2 left unassigned in the spectrum of 7,9-$B_9C_2H_{12}^-$ occurs at +5.4 ppm and this must be due to B(2,5). In conclusion, the ^{11}B NMR spectrum of 7,9-$B_9C_2H_{12}^-$ consists of six resonances of relative intensities 2:1:2:2:1:1, reading upfield, which can be assigned to B(2,5), B(8), B(3,4), B(10,11), B(6), and B(1), respectively.

This assignment of the ^{11}B NMR spectrum of 7,9-$B_9C_2H_{12}^-$ allows us to comment on the ^{11}B NMR spectra and probable structures of other substituted 7,9-$B_9C_2H_{12}^-$ ions which have been reported previously in the literature. It has been shown that Lewis bases such as $CH(CN)_2^-$ attack *closo*-2,3-$B_9C_2H_{11}$ possibly by a mechanism like the cage opening shown in Figure 2 to form $\{10\text{-}[CH(CN)_2]\text{-}7,9\text{-}B_9C_2H_{11}\}^-$.[16] The ^{11}B NMR spectrum of this anion contains seven discernible doublets (see Table I) indicating that substitution has introduced asymmetry into the molecule. The narrow doublet centered at 13.6 ppm (J_{BH} = 51 Hz) is assigned to the substituted boron atom which also displays additional bridge hydrogen coupling (J_{BH} = 50 Hz) strongly suggesting that the dicyanomethyl substituent is attached at B(10) or B(11). Attack of $CH(CN)_2^-$ at B(6) of 1,8-$B_9C_2H_{11}$ and cage opening as indicated in Figure 2 would generate the $\{10\text{-}[CH(CN)_2]\text{-}7,9\text{-}B_9C_2H_{11}\}^-$ ion.

Reaction of 2,3-$B_9C_2H_{11}$ with ethoxide ion generated the nido compound $B_9C_2H_{11}OC_2H_5^-$. The ^{11}B NMR spectrum of this anion is presented in Figure 4. The ethoxy-substituted boron resonance is the broad singlet at −1.2 ppm. Observation of the ^{11}B spectrum while decoupling the proton signal in the bridge region causes the singlet to sharpen. This indicates that the ethoxy group is substituted at B(10). In a previous study of the $B_9C_2(CH_3)_2H_9OC_2H_5^-$ ion generated in the same manner as outlined above it was proposed that the ethoxy group was attached at B(3).[15] A proton-decoupling experiment might provide evidence that this is a B(10)-substituted derivative as well.

In Figure 5 are presented the normal and line-narrowed 70.6-MHz ^{11}B NMR spectra of the adduct formed by reaction of $N(C_2H_5)_3$ with 2,3-$(CH_3)_2$-2,3-$B_9C_2H_9$. The two resonances at 9.7 and 21.5 ppm show a small splitting which is due to coupling with the bridge hydrogen as determined by a proton decoupling experiment. The two signals are therefore associated with B(10) and B(11). The signal at 9.7 ppm does not display terminal hydrogen coupling and is therefore the boron atom which has the $N(C_2H_5)_3$ group attached to it. This analysis suggests that the adduct is 10 substituted. In a previous study of $(CH_3)_3N{\cdot}B_9C_2H_{11}$, which was formed in the same manner as the triethylamine derivative described above, it was proposed that the Lewis base was attached at B(3).[15] This interpretation is based on the apparent secondary coupling on the doublet centered at 35.2 ppm (see Figure 7 of ref 15) which was attributed to bridge hydrogen coupling. The highest field multiplet (35 ppm) regions observed in the line-narrowed ^{11}B NMR spectra of both the trimethylamine and triethylamine adducts are very similar in character. One must be very cautious in the interpretation of line-narrowed spectra. A proton-decoupling experiment on the trimethylamine adduct might give evidence that this adduct is also B(10) substituted.

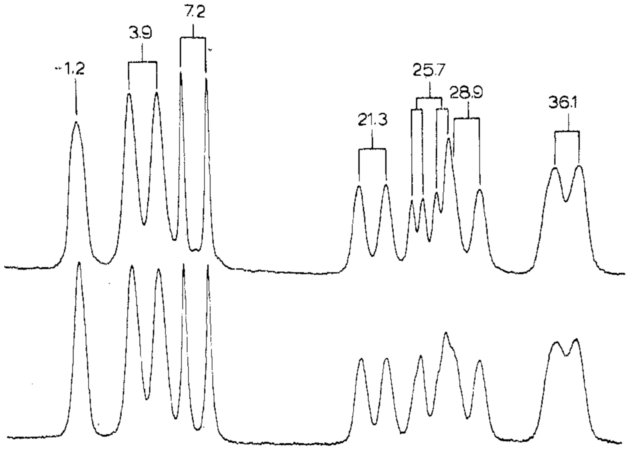

Figure 4. The 70.6-MHz ^{11}B NMR spectrum of $(CH_3)_4$N[10-C_2H_5O-7,9-$B_9C_2H_{11}$] in acetone solution. The lower trace is the bridge-proton-decoupled spectrum.

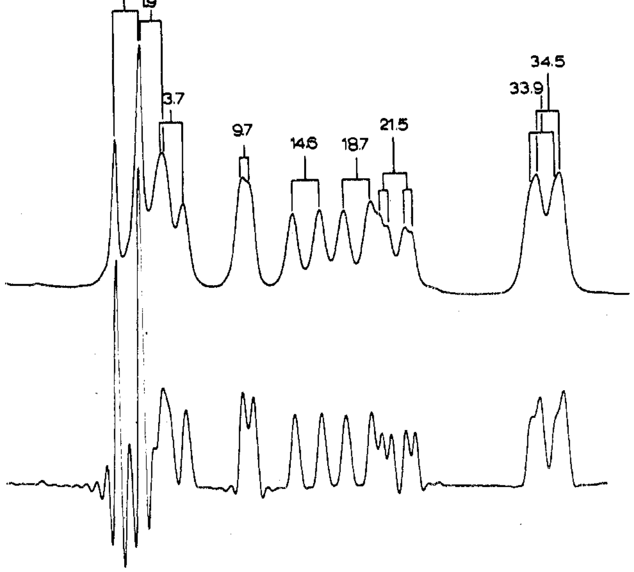

Figure 5. The 70.6-MHz ^{11}B NMR spectrum of 10-$(C_2H_5)_3$N-7,9-$B_9H_9C_2(CH_3)_2$ in acetone solution. The lower trace is a line-narrowed spectrum.

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Registry No. $(CH_3)_3$NH[7,9-$B_9C_2H_{12}$], 54531-56-5; $(CH_3)_4$N[1,6-Br_2-7,9-$B_9C_2H_{10}$], 54531-57-6; $(CH_3)_4$N[3,4-$O_2C_6H_4$-7,9-$(CH_3)_2$-7,9-$B_9C_2H_8$], 54531-54-3; Cs[3,4-$O_2C_6H_4$-7,9-$(CH_3)_2$-7,9-$B_9C_2H_8$], 54575-92-7; $(CH_3)_4$N{10-[$CH(CN)_2$]-7,9-$B_9C_2H_{11}$}, 54531-53-2; $(CH_3)_4$N[10-C_2H_5O-7,9-$B_9C_2H_{11}$], 54531-55-4; 10-$(C_2H_5)_3$N-7,9-$B_9H_9C_2(CH_3)_2$, 54484-51-4; 2,3-$B_9C_2H_{11}$, 17764-84-0; EtOH, 64-17-5; 2,3-dimethyl-2,3-dicarba-*closo*-undecaborane(11), 17764-85-1; $(C_2H_5)_3$N, 121-44-8; ^{11}B, 14798-13-1.

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Photochemical Study of the *N*-Methylborazines

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Photolysis of *N*-methylborazine with 1849-Å radiation yields H_2, CH_4, borazanaphthalene, *N*-methylborazanaphthalene, and *N*-dimethylborazanaphthalene. Photolysis of *N*-methylborazine in the presence of ammonia, methanol, or dimethylamine yields predominantly a B-monosubstituted derivative. The relative quantities of ortho to para isomers in the products were determined by NMR. The photochemical reactions of *N*-dimethylborazine and *N*-trimethylborazine with ammonia were also investigated. Suggested mechanisms for these reactions are discussed.

Introduction

In 1967 Lee and Porter reported the synthesis of *B*-aminoborazine in a gas-phase photochemical reaction of borazine with ammonia using 1849-Å radiation.[1] Other B-monosubstituted borazines, including *B*-methoxyborazine[2] and *B*-dimethylaminoborazine,[3] have also been prepared photochemically. In 1972, Neiss and Porter presented a quantitative analysis of the effect of 1849-Å radiation on borazine in the absence of a second reagent[4] and also reported on a quantum yield study of the borazine–ammonia reaction.[5] The early 1970's showed an upsurge of interest in the characterization of *N*-methylborazine derivatives,[6-10] due in part to the development of a facile large-scale synthesis and purification procedure for the *N*-methylborazines by Beachley.[11] The uv absorption spectrum of *N*-trimethylborazine has been published[12] and is similar to that of borazine, except that its maximum is red shifted (ϵ_{max} 1650 Å for borazine, 1860 Å for *N*-trimethylborazine). A number of theoretical studies have been reported on this compound[8,12-17] and on *N*-methylborazine and *N*-dimethylborazine.[18] These studies predict an increase in electron density on the boron atoms adjacent to the *N*-methyl group, relative to the parent borazine molecule. The present paper attempts to probe the effect of this methyl substitution on the photochemical reaction mechanism of the *N*-methylborazines.

Experimental Procedures

The *N*-methylborazines were prepared from $NaBH_4$ (Alpha Chemical Co.) and CH_3NH_3Cl and NH_4Cl (Fisher Scientific) under a helium atmosphere using $NaBH_4$-dried dimethoxyethane (Eastman Chemicals) as solvent, according to the method of Beachley.[11] The mixture of borazine and all the possible *N*-methylborazines was purified by gas chromatography (acid-washed firebrick with 15% Apiezon). *N*-Trimethylborazine, prepared separately by similar reaction of CH_3NH_3Cl and $NaBH_4$, was purified by vacuum distillation through traps maintained at −23, −80, and −196°. The −23° trap contained pure *N*-trimethylborazine while the −80° trap contained some of this compound and the dimethoxyethane solvent. *B*-Trideuterio-*N*-trimethylborazine was prepared by the photolysis of D_2 (Matheson, reagent grade) with *N*-trimethylborazine.[19] Methyl alcohol (Mallinckrodt) and ammonia and dimethylamine (Matheson) were distilled prior to use and were analyzed for purity by ir and mass spectra.

The photolysis cell for study of *N*-methylborazine was a 500-ml vessel (Figure 1) equipped with a quartz immersion well which transmitted light down to 1800 Å. The photolysis chamber was separated by a stopcock from a 100-ml bulb used to collect noncondensable product gases. Reactions were run for 1 hr with *N*-methylborazine pressures ranging from 2 to 5 mm, using a Hanovia medium-pressure mercury lamp purged with dry N_2. The photolysis vessel was cooled to liquid nitrogen temperatures after the photolysis and the noncondensable products expanded into the 100-ml bulb. Mass spectra were taken of the noncondensable products. The material remaining in the photolysis vessel was pumped through traps maintained at −45, −80, and −196°. The contents of these traps were analyzed mass spectrometrically.

Mixtures of *N*-methylborazine and a second reagent (NH_3, CH_3OH, or $NH(CH_3)_2$) were photolyzed for about 1 hr in a 2-l. vessel. Typical reactant pressures were in the range 2–3 mm *N*-methylborazine and 2–10 mm reagent, with total pressures ranging from 4 to 12 mm. *N*-Dimethylborazine–ammonia mixtures (ratio 1:5, total pressure 12 mm) were also photolyzed. The photolysis products were pumped through traps maintained at −45, −80, and −196°. The contents of the −45° trap were analyzed by ir, mass, and proton NMR spectra.

N-Trimethylborazine–ammonia mixtures were photolyzed for 30 min and volatile products collected in a −23° trap. Nonvolatile crystalline products found on the walls of the photolysis vessel were soluble in $CDCl_3$. In one experiment ND_3 was photolyzed with *B*-trideuterio-*N*-trimethylborazine. For this reaction the vacuum-line manifold was preconditioned with ND_3 before the measured reagents were added. *B*-Amino-*N*-trimethylborazine, a product from the reaction of ammonia with *N*-trimethylborazine, was photolyzed for 30 min in a photolysis vessel saturated with mercury vapor. Crystalline products deposited on the walls of the reaction vessel and the contents of the traps from all of these reactions were analyzed by mass, infrared, and proton NMR spectra.

Infrared spectra were taken on a Perkin-Elmer 521 Grating spectrophotometer with gas samples in a 10-cm cell or with mulls between two NaCl plates. Mass spectra of gas samples were obtained using a CEC 21-103A mass spectrometer, while those of solid samples