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SYNTHESSES AND CHARACTERIZATION OF BH₂NH₂ SPECIES

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

by

Cecil William Hickam, Jr., B.S.

The Ohio State University
1964

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I. INTRODUCTION

A. General Background

Because boron chemistry had been limited to research on boric acid and borates, Stock, in 1912, decided to investigate unexplored areas of boron chemistry, such as the hydrides. His investigations were rewarding, for by 1933 he had isolated the boron hydrides: diborane-6 (B₂H₆), tetraborane-10 (B₄H₁₀), pentaborane-9 (B₅H₉), pentaborane-11 (B₅H₁₁), hexaborane-10 (B₆H₁₀), and decaborane-14 (B₁₀H₁₄) (1). Although his work produced new and interesting compounds, they possessed structures which were not explicable in terms of the then existent ideas of structural chemistry. Only within recent years has sufficient information been available, so as to be able to discuss, intelligently, the bonding of the boron hydrides.

It is remarkable that Stock was able to make contributions to boron chemistry, since materials available were limited at the time of his researches. Not only was he restricted to the use of soft glass, a difficult substance with which to work and a substance which cannot stand sudden thermal shocks, but he had to use mercury-valves instead of lubricated stopcocks because of the lubricant's sensitivity...
to boron hydrides. However, in spite of these difficulties, Stock not only contributed to boron hydride chemistry, but was responsible for the development of chemical vacuum line techniques. Many of the techniques and procedures used today have originated from Stock's work.

The simplest of the boron hydrides, diborane-6, henceforth called diborane, is a bridged structure (2). The four terminal hydrogens define a rectangular plane which contains

The two boron atoms and the two bridged hydrogens lie above and below the plane, respectively.

Several descriptions of the bonding in diborane have been given. The most popular of these is that of Eberhardt, Crawford, and Lipscomb (3), who assumed each boron to be an \(sp^3\) hybrid. The in plane hydrogens form classical electron pair bonds. The \(sp^3\) hybrids, which are directed above and below the plane, and the \(s\) orbitals of the hydrogens in the bridge mutually overlap, forming two three-centered orbitals, each containing two electrons—one from the hydrogen and one
from one of the borons. The bridge bond has been called a three-centered or "banana bond."

![Diagram of Boron Hydride]

That BH$_3$ is not a stable entity is attributed to the fact that in all of the known boron hydrides boron tends to employ all of its low-lying orbitals in bond formation. In diborane, this is accomplished through the formation of the hydrogen bridges; thus all four valence orbitals of boron are occupied. Lewis bases can displace the bridge hydrogens to form molecular addition compounds. In fact, diborane behaves as a Lewis acid. Typical reactions which have been observed are these (4):

- \[ \text{B}_2\text{H}_6 + 2\text{Me}_3 \rightarrow 2\text{H}_2\text{BNMe}_3 \]
- \[ \text{B}_2\text{H}_6 + 2\text{Me}_2\text{O} \rightarrow 2\text{H}_2\text{BOMe}_2 \]
- \[ \text{B}_2\text{H}_6 + 2\text{CO} \rightarrow 2\text{H}_3\text{BOO} \]

In 1926 Stock and Pohland (5) prepared an ammonia-diborane addition compound, which had an empirical formula of B$_2$H$_6$ 2NH$_3$, the so-called diammoniate of diborane. Pyrolysis of this compound produced a 30 percent yield of borazine, B$_3$N$_2$H$_6$. Eleven years later, by means of an electron diffraction study, Bauer proved that borazine is a structural analogue of benzene because it is a planar, six
membered ring (6). Since borazine is isoelectronic as well as structurally analogous to benzene, it has been called inorganic benzene (7); the following Kekule' structures have been proposed (8):

\[
\begin{array}{c}
\text{HN} \\
\text{B} \\
\text{NH} \\
\end{array}
\quad \quad \quad \quad 
\begin{array}{c}
\text{HN} \\
\text{B} \\
\text{NH} \\
\end{array}
\quad \quad \quad \quad 
\begin{array}{c}
\text{HN} \\
\text{B} \\
\text{NH} \\
\end{array}
\]

Contrary to early belief, there is little evidence of aromatic character in the borazine system (9,10). Chemically, it behaves as though it has the following structure, in which electron pairs are localized on the nitrogen.

\[
\begin{array}{c}
\text{H} \\
\text{B} \\
\text{HN:} \\
\text{BH} \\
\text{NH} \\
\end{array}
\quad \quad \quad \quad 
\begin{array}{c}
\text{H} \\
\text{B} \\
\text{NH} \\
\end{array}
\]

Unlike benzene with its delocalized \( \pi \) electron system, borazine forms addition compounds readily. Thus, for example, a complex in the mole ratio 1:3 is formed with...
HCl, in which a proton adds to a donor atom, nitrogen, and a chloride adds to an acceptor atom, boron (7,11).

\[
3 \text{HCl} + \text{B}_3\text{N}_3\text{H}_6 \rightarrow \text{ClBH}_2 \text{NMe}_2 \rightarrow \text{Me}_2\text{N:} \rightarrow \text{BH}_2
\]

Since the B-N bond is isoelectronic with the C-C bond, many investigations have been carried out to prepare analogues of organic compounds. In addition to substituted borazine compounds, many analogues of ethane and ethylene have been prepared. The ethylene derivatives frequently polymerize to give, in general, four and six membered rings, which through the unshared electron pair of nitrogen forms an intermolecular dative bond with a boron atom.
The ethylene derivatives are called aminoboranes. For example, Me₂NBHMe is named dimethylaminomethylborane. Cyclic aminoborane, containing alternating B-N bonds are called cycloborazanes. For example, (MeHNBH₂)₃ is named N, N', N''-trimethylcyclotriborazane. If it is not known whether the compound has a cyclic or chain-like structure, it is referred to as an aminoborane and the degree of polymerization is noted if this fact is known. The cyclic compounds contain coordinately saturated borons and nitrogens and are highly resistant to attack by protonic compounds such as water and hydrogen chloride. On the other hand, the acyclic compounds form addition compounds with protonic substances.

\[
\text{Me}_2\text{B-} \text{NH}_2 + \text{HCl} \rightarrow \text{MeB-N-H} \quad \text{Cl}
\]

Inductive and steric effects appear to determine the degree of polymerization of aminoboranes to form cycloborazanes (12,13). On polymerization, the strength of the intermolecular B-N bond formed is related to the inductive effect of the substituents on the boron and the nitrogen, the strength of the bond being greater with more electronegative substituents on boron and more electropositive substituents on nitrogen. This increases the boron's
electron acceptor properties and the nitrogen's electron donor properties. For example, dimethylaminoborane has a greater tendency to dimerize than aminodimethylborane because the B-N intermolecular bond formed in the former is stronger since methyl groups are more electropositive than hydrogens. Since ethyl substituents are more electropositive than methyl groups, diethylaminodichloroborane would be expected to polymerize more easily than dimethyldichloroborane, but the opposite is the case. It is believed that the inductive effect is overcompensated by the steric effect caused by the ethyl groups (13). The ability to form dimers, trimers, and higher polymers is dependent on steric effects. The larger the size of the polymer the less available space there is for the substituents (13). For example, dimethylaminodimethylborane is a monomer, dimethylaminoborane is a dimer, and methylaminoborane is a trimer, and aminoborane forms higher polymers.

At this point it is of interest to consider the charge separation in the B-N bond in aminoboranes and cycloborazanes. Applying the formalism of the valence bond theory, aminoboranes are represented as

\[ \text{H}_2\text{B}^- + \text{NH}_2 \]

and cycloborazanes are represented as

\[ \begin{array}{c}
\text{R}_2\text{N} \\
\text{B} \\
\text{H}_2
\end{array} \quad \begin{array}{c}
\text{+} \\
\text{N} \\
\text{R}_2
\end{array} \]
However, recent work of Hoffmann (14), using the extended
Huckel theory, indicates that although there is some trans-
fer of electronic charge from nitrogen to boron in such
compounds, the net negative charge on nitrogen is signifi-
cantly larger than that on boron. Therefore, formal
representations, such as those given above, are misleading.

One of the general methods for preparing aminoboranes
is the dehydrogenation of the corresponding amineborane,
RR'HBNXX'H, which occurs because of the interaction of the
hydridic hydrogen on boron with the protonic hydrogen on
nitrogen to form hydrogen.

\[
\text{MeH}_2\text{NBH}_2 \rightarrow \frac{1}{3}(\text{MeHNBH}_2)_3 + \text{H}_2
\]

The same mechanism has been applied for the formation of bora-
zine, which involved the following condensation chain (12).

\[
\frac{1}{2} \text{B}_2\text{H}_6 + \text{NH}_3 \rightarrow \text{BH}_3\text{NH}_3 \rightarrow \text{BH}_2\text{NH}_2 \rightarrow \text{BHNH} \rightarrow \text{B}_3\text{N}_3\text{H}_6
\]

However, recent work in this laboratory has shown that bora-
zine is not synthesized by the pyrolysis of ammoniaborane,
H$_3$BNH$_3$ (15).

The preparation of methyl derivatives of aminoborane
has been accomplished by the following general methods of
synthesis.

\[
\text{R}_3\text{N} + \text{BR'}_3 \rightarrow \text{R}_2\text{NBR'}_2 + \text{RR'}
\]

\[
\text{MBR'}_4 + \text{NR}_2\text{HCL} \rightarrow \text{MCL} + \text{RR'} + \text{H}_2 + \text{R}_2\text{BNR}_2
\]

\[
2\text{RMgBr} + \text{R'}_2\text{NBCL}_2 \rightarrow \text{R'}_2\text{NBR}_2 + \text{MgCl}_2 + \text{MgBr}_2
\]

(R and R' = H or Me; and R$_3$N, for example, can be Me$_2$NH)
Dimethylaminodimethylborane, Me$_2$BNMe$_2$, has been prepared by heating tetramethyldiborane with dimethylamine at 100°C. (16). A second method involves treating Me$_2$BBr with dimethylamine. This compound is a monomer, melting at -92°C. As a liquid, at room temperature, it does not polymerize, even after standing for months.

Methylaminodimethylborane, MeHNMe$_2$, is prepared by heating trimethylboron with methylamine at 310°C. and 20 atmosphere (17). It is a monomer with a boiling point of 38°C. At room temperature it reacts with hydrogen chloride to give the addition compound, Me$_2$ClB(NH$_2$)$_2$Me, a non-volatile solid. Heating MeHNMe$_2$ to 450°C gives hexamethylborazine and methane.

While MeHNMe$_2$ is a monomer, its isomer, dimethylaminomethylborane, Me$_2$NBHMe, is monomeric in the gaseous state, but to a large extent it is dimeric in the liquid state at room temperature (18). It is synthesized by the addition of B, B'-dimethyldiborane, (MeBH$_2$)$_2$, to dimethylamine at -78°C. Monomeric Me$_2$NBHMe exists in equilibrium with dimeric dimethylaminoborane and dimethylaminodimethylborane.
Dimethylaminoborane, \( \text{Me}_2\text{NBH}_2 \), was prepared by Wiberg in 1948 (12) through the pyrolysis of dimethylamineborane at 180-200°C. At room temperature it is a solid, containing dimeric species, but at higher temperatures there is an equilibrium between the dimeric and monomeric forms. At 30°C, ninety per cent of it is dimeric and at 105°C, ninety per cent of it is monomeric. The equilibrium constant for the reaction, \( \text{Me}_2\text{NBH}_2 \leftrightarrow (\text{Me}_2\text{NBH}_2)_2 \), has been shown to be \( \log_{10} K(\text{atm.}) = 11.126 - (4533/T) \) by Burg and Randolph, after taking into consideration the fact that the only side reaction seriously disturbing the monomer-dimer equilibrium was the disproportionation, \( \text{Me}_2\text{NBH}_2 \rightarrow (\text{Me}_2\text{NBH}_2)_2 \rightarrow \text{Me}_2\text{WB}_2 + \text{Me}_2\text{NBH}_2 \) (19). They were also able to isolate the very volatile addition compound, \( \text{Me}_2\text{NBH}_2\text{NMe}_3 \), which could be fractionated through a -60°C. trap, by heating a mixture of \( \text{Me}_2\text{NBH}_2 \) and trimethylamine at 140°C. Other preparations of dimethylaminoborane involve the room temperature reaction of lithium borohydride with dimethylammonium chloride in ether (20) and by heating diborane under pressure with bis(dimethylamino) borane or tris(dimethylamino) borane (19).

Trimeric dimethylaminoborane is formed by heating the dimer with pentaborane-9 at 100-110°C. (21). It melts at 97°C. and is unaffected by moist air. Trefonas and Lipscomb (2) determined the structure by means of a
three-dimensional X-ray analysis and found it to be a chair configuration.

\[ \text{Me}_2 \text{N} \text{Me} \]

\[ \text{Me}_2 \text{B} \text{H}_2 \text{NMe}_2 \]

Aminodimethylborane was prepared by Wiberg and co-workers through pyrolysis of ammonia-trimethylborane at 280°C. and 20 atmospheres. The use of higher temperatures (320-340°C.) gave B, B', B''-trimethylborazine and methane. Monomeric aminodimethylborane (b. p. 4°C.) formed a dimeric solid (m.p. 9°C.) on cooling as at -19°C. and 76 mm. Hg twelve per cent of the molecules are dimeric (23,24).

Pyrolysis at 100°C. of methylamine-borane produced N, N', N''-trimethylcyclotriborazane as shown by molecular weights in benzene, nitrobenzene, and ammonia (25). This compound is stable in moist air and sublines at 100°C.

Pyrolysis of O, N-dimethylhydroxylamineborane gives much lower yields (25). This cyclotriborazane was prepared by Gaines and Schaeffer (26) through the room temperature reaction of methylamine hydrochloride with sodium borohydride and by the reaction of the tri-hydrochloride adduct of N, N', N''-trimethylborazane and sodium borohydride. Fractional
crystallization procedures in benzene and methanol separated two isomers. On the assumption that it has a chair configuration, the physical properties indicate that one isomer has all three methyl groups equatorial in the chair configuration, and that the other isomer has two equatorial methyl groups and one axial methyl group in the chair configuration.

A series of aminodiarylboranes was prepared by Coates and Livingstone (27) through the following methods:

\[
\begin{align*}
\text{Ar}_2\text{BCl} + \text{LiNH}_2 & \longrightarrow \text{Ar}_2\text{BNR}_2 + \text{LiCl} \\
\text{Ar}_2\text{BCl} + \text{R}_2\text{NH} + \text{Et}_3\text{R} & \longrightarrow \text{Ar}_2\text{BNR}_2 + \text{Et}_3\text{NHCl} \\
2\text{ArMgBr} + \text{Cl}_2\text{BNR}_2 & \longrightarrow \text{Ar}_2\text{BNR}_2 + \text{MgCl}_2 + \text{MgBr}_2
\end{align*}
\]

All the aminodiarylboranes—\(\text{Ph}_2\text{BNMe}_2\), \((\text{p-MeC}_6\text{H}_4)_2\text{BNMe}_2\), \(\text{Ph}_2\text{BNPh}_2\), \((\text{p-BrC}_6\text{H}_4)_2\text{BNMe}_2\), \(\text{Ph}_2\text{BN(C}_6\text{H}_4\text{Me-p})_2\), and \((\text{p-MeC}_6\text{H}_4)_2\text{BNPh}_2\)—which have been synthesized are monomeric with the exception of \(\text{Ph}_2\text{BNH}_2\), which is a dimer and non-polar in benzene solutions. The methyl derivative of aminodiphenylborane, \(\text{Ph}_2\text{BNHMe}\), changes from a monomer to a dimer at room temperature (28). It was observed that aminodiarylboranes, \(\text{Ar}_2\text{BNR}_2\), are dimeric when \(R = \text{H}\), but are monomeric when \(R = \text{alkyl or aryl}\); however when the group in the ortho position of the aryl group is other than hydrogen, then the compound is monomeric, due to steric hindrance.

For example, aminodi-o-totyl borane and aminodimesitylborane are monomers.
Niedenzu and Dawson (29) prepared (di-sec-butylamino) diethylborane, (dicyclohexylamino) dimethylborane, (ethylphenylamino) diethylborane, (ethylphenylamino) diphenylborane, (methylphenylamino) dimethylborane, (methlnaphthylamino) dimethylborane, and (ethylphenylamino) di-p-tolylborane by the reaction of an appropriate Grignard compound and an N-disubstituted aminodichloroborane. All of these compounds are monomers.

Di and trialkyl silanes have been used to prepare aminoboranes (30,31).

\[
\begin{align*}
\text{Et}_2\text{NCl}_2 + \text{Me}_2\text{SiH}_2 & \xrightarrow{200^\circ\text{C.}} \text{Et}_2\text{NBH}_2 \\
\text{Et SiH} + \text{Me}_2\text{NBR}_2 & \xrightarrow{\text{Rm. Temp.}} \text{Me}_2\text{NBHBr}
\end{align*}
\]

Dimethylaminodichloroborane, \( \text{Me}_2\text{NCl}_2 \), has been prepared according to the following equation (21):

\[
P(\text{NMe}_2)_3 + 3\text{BCl}_3 \rightarrow \text{PCl}_3 + 3/2 (\text{Me}_2\text{NCl}_2)_2
\]

The liquid is a monomer which dimerizes to a solid after standing for several days (16,32). Warming the liquid in vacuum produces dimeric dimethylaminodichloroborane more rapidly.

The following exchange reaction has been observed:

\[
\text{Me}_2\text{NCl}_2 + \text{MeNBMMe}_2 \xrightarrow{170^\circ\text{C.}} \text{Me}_2\text{NBMeCl}
\]

Dimethylaminomethylchloroborane does not show any sign of disproportionation; it slowly forms a dimer (33).
Hexamethylborazine forms a 1:3 solid adduct with hydrogen chloride at 20-80°C. which decomposes at 15°C. to the gaseous monomer, methylaminochloromethylborane, (MeClBNHMe). Cooling the monomer causes formation of the solid dimer (17).

Aminohaloboranes have been prepared at the U. S. Borax Company using the following reaction (34):

\[ \text{PhBCl}_2 + \text{Me}_2\text{NH} + \text{Et}_3\text{N} \longrightarrow \text{Et}_3\text{NHCl} + \text{ClPhBNMe}_2 \]

Dimethylaminodifluoroborane (m. p. 165-168°C.) is a monomer and is prepared by the following reactions:

\[ \text{Me}_2\text{NH} + \text{BF}_3\cdot\text{Et}_2\text{O} \longrightarrow \text{Me}_2\text{NBF}_2 + \text{HF} + \text{Et}_2\text{O} \quad (35) \]

\[ \text{BF}_3 + \text{Me}_2\text{BNMe}_2 \longrightarrow \text{Me}_2\text{NBF}_2 \quad (36) \]

Highly polymeric aminodifluoroborane, H$_2$NBF$_2$, has been reported, but no details have been published as yet (37).

While many of the derivatives of aminoborane, BH$_2$NH$_2$, have been prepared, as indicated in the earlier discussion, only limited work has been reported on the preparation and characterization of BH$_2$NH$_2$ species.

Hornig, Jolly, and Schaeffer (38,39) studied the reaction of the diammoniate of diborane with trimethyl amine. From vapor pressure studies in liquid ammonia, they claimed the aminoborane to be a trimer.

\[ \text{B}_2\text{H}_6\cdot2\text{NH}_3 + \text{Me}_3\text{N} \longrightarrow \text{NH}_3 + \text{H}_2 + \text{Me}_3\text{NBH}_3 + \frac{1}{3}(\text{BH}_2\text{NH}_2)_3 \]
Schlesinger, Ritter, and Burg (40) were the first to report the preparation of aminoborane in 1938 by the decomposition of aminodiborane.

\[ 2B_2H_7N \xrightarrow{\text{Rm. Temp.}} B_2H_6 + \frac{1}{x}(BH_2NH_2)x \]

But this was based on the recovery of diborane and they made no further attempts to identify or characterize the solid products.

Wiberg, Bolz, and Buchheit (12) formed aminoborane by the reaction of diborane with ammonia at 100°C.

\[ B_2H_6 + 2NH_3 \xrightarrow{100°C} \frac{1}{x}(BH_2NH_2)x + H_2 \]

They reported the solid aminoborane to polymeric and non-volatile. When heated, it decomposed to a compound resembling boron nitride.

Metallic sodium reacts with diammoniate of diborane, \( (BH_2(NH_3)_2)(BH_4) \), in liquid ammonia to form aminoborane (41). The aminoborane isolated from the reaction was reported to be amorphous, as indicated by X-ray powder diffraction patterns, and the reaction also revealed that the aminoborane had undergone ammonolysis.

\[ BH_2NH_2 + xNH_3 \rightarrow BH_{2-x}(NH_2)_1+x + xH_2 \]

Schaeffer and Basile prepared aminoborane by the reaction of lithium amide with diborane in diethyl ether (42). It was reported to be amorphous and to be insoluble in diethyl ether.
In a review article (45), Burg stated the belief, which in general has been accepted without question, that "The polyethylene analogue \( (H_2\text{NBH}_2)_x \) forms crosslinks very easily, with spontaneous loss of hydrogen so that if one heats it the trend is toward the HNBH high polymers and eventually boron nitride."

B. Statement of Problem

Species of empirical composition \( BH_2\text{NH}_2 \) are the least characterized compounds in the boron-nitrogen system. Substances of this composition have been reported to be essentially intractable, highly polymeric, amorphous materials which split out hydrogen easily (12,40,41,42). Methods for producing the so-called highly polymeric \( BH_2\text{NH}_2 \) have been based on the preparation of \( BH_2\text{NH}_2 \) units, which undergo association through formation of intermolecular dative bonds. The following reactions have been reported:

\[
\begin{align*}
B_2H_6 + 2NH_3 & \xrightarrow{100^\circ C} \frac{1}{x}(BH_2\text{NH}_2)_x + H_2 \\
B_2H_5\text{NH}_2 & \rightarrow \frac{1}{x}(BH_2\text{NH}_2)_x + \frac{1}{2}B_2H_6 \\
(BH_2(NH_3)_2)(BH_4) + Na & \xrightarrow{\text{liq. } NH_3} \frac{1}{x}(BH_2\text{NH}_2)_x + NH_3 + \frac{1}{2}H_2 + NaBH_4 \\
B_2H_6 + LiNH_2 & \xrightarrow{Et_2O} \frac{1}{x}(BH_2\text{NH}_2)_x + LiBH_4
\end{align*}
\]

It has not been established that the \( BH_2\text{NH}_2 \) products from these reactions are identical, nor has it been shown that the products are not mixtures of several forms of \( BH_2\text{NH}_2 \),
representing different degrees of association. Since, in principle, the association process of $\text{BH}_2\text{NH}_2$ could lead to the formation of a variety of species which have not been reported previously in the boron-nitrogen system, a thorough investigation was undertaken to study the syntheses and properties of aminoborane. Not only were previous syntheses of aminoborane re-examined, but new avenues for the synthesis of aminoborane were followed. The approach taken for the re-examination of the aminoborane system involved (1) the formation of aminoborane from reactions of diammoniate of diborane with bases in ammonia, since the reaction of diammoniate of diborane with sodium in ammonia had been reported to yield $\text{BH}_2\text{NH}_2$ species, (2) a re-examination of Schaeffer and Basile's work (42) in which aminoborane was formed from the reaction of lithium amide with diborane in diethyl ether, (3) a study of the reaction of diborane with different alkali amides and a study of the reaction of lithium amide-diborane using different ether solvents was also undertaken.
II. EXPERIMENTAL

A. Apparatus

1. Vacuum system

Because of the extreme sensitivity to moisture and air, all materials used in this study were handled in a standard vacuum system similar to that described by Sanderson (44). The vacuum apparatus consisted of the following main components: (1) a pumping section; (2) a main manifold; (3) two reaction trains; one of which had a two liter metal cylinder attached to it in order to accommodate large volumes of gaseous products or reactants; (4) a distillation train; (5) two five-liter metal storage cylinders; and (6) a calibrated Toepler system with its own distillation train. Pressures were measured by means of mercury manometers. Volumes of the components of the system were determined using carbon dioxide as the measuring agent.

a. Pumping section

The pumping system consisted of a high capacity Duo-Seal forepump and a mercury diffusion pump filled with triple distilled mercury. Cold traps cooled with liquid nitrogen preceded the diffusion pump and the forepump. The diffusion pump could be by-passed when necessary to avoid oxidation and
and contamination of the mercury. Using the forepump only, a low pressure of $10^{-3}$ mm. of Hg could be obtained; while pumping with both the forepump and mercury diffusion pump "in series," a low pressure of at least $10^{-5}$ mm. of Hg could be obtained consistently.

b. Reaction train

Reaction trains were used to introduce volatile materials into the vacuum line as well as for carrying out chemical reactions. The reaction trains contained several reaction stations consisting of a 14/35 $\frac{\text{male}}{}$ joint separated from the reaction manifold by a 2 or 4 mm. vacuum stopcock. On each such station there was a mercury "blowout" between the joint and the stopcock. Each reaction train was connected to the main manifold and to the distillation train. To one of the reaction trains was connected a two-liter cylinder by means of a stopcock, which had a U-tube trap and a mercury manometer. This reaction train was connected directly to the Toepler system to facilitate the measurement of non-condensable gases; it had one 14/35 $\frac{\text{female}}{}$ joint which was horizontally attached to it, for the purpose of attaching a vacuum line extractor to the reaction train.

c. Distillation train

The distillation train was used for low temperature fractionation of volatile mixtures and for measuring out,
volumetrically, gases, mainly diborane. It consisted of four calibrated traps of a total volume of over half a liter. A mercury manometer was connected to one of the traps for measuring pressure.

d. Storage system

For storage of condensable gases a five-liter cylinder was used, which was connected to a mercury manometer and a U-trap. Each cylinder was connected to the distillation train manifold by a Stock type mercury float valve to prevent, during storage, contact of the gas with any stopcock lubricant. A vacuum stopcock was placed between the mercury float valve and distillation train manifold. The condensable gases stored in the storage system never exceeded a pressure of one atmosphere at room temperature.

e. Toepler system

The Toepler system was used for measuring, volumetrically, quantities of non-condensable gases. It was connected to one of the reaction trains by means of a vacuum stopcock and had a self-contained distillation train, which consisted of two U-tube traps preceding the pump. The U-tube traps were used to remove condensable gases by immersing them in liquid nitrogen. The gas burette which was connected to the Toepler pump was divided in two sections by means of a three-way stopcock. One part of maximum volume of 125 ml. was used for measuring small
amounts of non-condensable gases; the second part contained a 100 ml. bulb joined to the stopcock by a 14/35 joint. Pressures were measured by a mercury manometer connected to the gas burette. The three-way vacuum stopcock made it possible to remove the gas in the Toepler system by way of the reaction train manifold or by way of the main manifold.

An auxiliary vacuum system, made of 1/4 inch copper tubing, was used to lower the Hg level in the float valves and the Toepler pump.

2. Molecular weight studies in liquid ammonia

Molecular weights were determined in liquid ammonia by cryoscopy. A typical experiment involved distilling and condensing a weighed amount of ammonia in the freezing point cell on the vacuum line. By using a platinum resistance thermometer, the freezing point (in ohms) of the ammonia was determined from a time-temperature cooling curve. After removal of the ammonia from the freezing point cell by distillation, a weighed sample of the compound under study was added to the freezing point cell. If the compound was sensitive to moist air, it was added to the cell under the inert nitrogen atmosphere of a dry box. The ammonia was redistilled into the cell and the freezing point (in ohms) of the solution determined from a time-temperature cooling curve.
Using the theoretical value, obtained from heat of fusion data, of 0.956°C./molal (45) for the cryoscopic constant of ammonia, the molecular weight of the compound was determined by the equation,

\[ M = \frac{K_f \times 1000 w_2}{\Delta T w_1} \]

In the above equation,
- \( M \) = molecular weight
- \( K_f \) = cryoscopic constant
- \( w_1 \) = grams of solvent
- \( w_2 \) = grams of solute
- \( \Delta T \) = freezing point of ammonia minus freezing point of solution.

The platinum resistance thermometer used had a \( \frac{dR}{dT} \) value of 0.1040 ohms per degree.

a. Freezing point cell

The freezing point cell is illustrated in Figure 1. It consists of two parts, the cap and the tube portion. A similar freezing point cell has been described by B. Z. Egan (46).

b. Stirrer system

To maintain homogeneity the solution was stirred by means of a spiral stirrer. The spiral stirrer was activated by means of a solenoid, which was placed around an iron rod that is sealed to 3 mm. glass tubing. The 3 mm. glass tubing
was connected to the spiral stirrer. In order to provide regular stirring the solenoid was connected to a microswitch, which was activated by a triangular cam. The cam was connected by a shaft to a 50 r.p.m. synchronous motor that activated the switch at 90 contacts per minute. The amount of voltage supplied to the solenoid to move the stirrer is controlled by a Variac.

c. Cryostat and cooling system

The cryostat and cooling system are illustrated in Figure 2. For the molecular weight determinations in liquid ammonia a methylene chloride slush bath was used as the refrigerant. Skelly Solve F was used to obtain thermal contact between the cell, E, and the double-walled vessel, C. Skelly Solve F was also used inside the thermometer well, H.

d. Thermometer

A platinum resistance thermometer was used, which had a temperature coefficient of resistance of 0.1040 ohm per degree Centigrade. It was a four-lead, potential-terminal type thermometer (Leeds and Northrup List No. 8064). The temperature sensitive platinum wire element is wound strain-free on a mica cross and sealed in a helium-filled platinum tube. The platinum tube is 5.5 mm. outside diameter, and 6 cm. overall length, with four platinum leads 3 inches long. The sensitive portion is about 3.5 cm. long.
Fig. 1.—Freezing Point Cell for Ammonia
Freezing point cell for ammonia
Fig. 2.—Cryostat and Cooling System
Cryostat and cooling system

A - Dewar, 12 cm. x 20 cm.
B - Slush bath for cooling the cell.
C - Double walled vessel which can be evacuated.
D - Liquid to insure good contact between the walls of the freezing paint cell and the double walled vessel.
E - Outer wall of the freezing point cell.
F - Solution which is being frozen.
G - Stirrer
H - Thermometer well.
J - Cork
K - Asbestos
e. Resistance bridge and accessories

A Mueller temperature bridge (Leeds and Northrup List No. 8069) was used to measure the resistance of the platinum thermometer. A detailed description of it is given in Leeds and Northrup Direction Book 77-2-1-1. A mercury cup commutator allowed reversing the connections to the thermometer for canceling the effects of lead resistance.

The bridge current was supplied by five nickel-cadmium batteries connected in series.

Qualitative current flow was detected with a L'Arsonval type galvanometer (Leeds and Northrup No. 2500).

3. Molecular weight studies in dimethyl sulfoxide

The freezing point cell used for molecular weight determinations by cryoscopy in dimethyl sulfoxide (m. p. = +18.45°C.) was very similar to that used for liquid ammonia, except a Beckmann thermometer was used to measure the freezing point depression. The freezing point cell is illustrated in Figure 3. A typical experiment is described on pages 43-45.

The cryostat and stirring system was the same as previously described for molecular weight studies in liquid ammonia.
Fig. 3.--Freezing Point Cell for Dimethyl Sulfoxide
Freezing point cell for DMSO
4. **Extractor**

The vacuum line extractor, illustrated in Figure 4, was used to separate moisture-sensitive compounds that had different solubility properties. The extractor was connected to the vacuum line by means of its side arm. In the case of an ammonia extraction, the top 24/40 Ø joint of the extractor was connected to a 24/40 Ø joint plug and the bottom 24/40 Ø joint connected to a tube or bulb, which was fitted with a 24/40 Ø joint. By filling the well with a Dry Ice-isopropyl alcohol bath, ammonia was condensed on the glass frit, which contained the sample to be extracted or washed. The ammonia solution was filtered by closing the stopcock on the extractor and by allowing the ammonia to warm and build up a pressure. The pressure of the ammonia then forced the solution through the frit and into the filtrate tube or bulb. The filtrate tube or bulb was immersed in a Dry Ice-isopropyl alcohol bath to maintain a lower pressure in the chamber below the frit than the chamber above the frit. The ammonia was removed by distillation or distilled and condensed again on the frit for another extraction or washing.

The extractor could also be used for reactions whose products had different solubility properties. Both of the extractor's 24/40 Ø joints were connected to bulbs which were fitted with 24/40 Ø joints. With the extractor in the
Fig. 4.—Extractor
14/35  

Side view of side arm

Well

Glass frit

24/40  

Extractor

2 mm. vacuum stopcock
opposite vertical position as used for the ammonia extraction experiment, the reaction was run in the bulb connected to the extractor. After the reaction was over the extractor was inverted; thus the side arm of the extractor served a dual role. The products were then washed or extracted in a similar manner as that described for the ammonia extraction.

5. Handling of products

Most reactions were carried out in tubes or bulbs which were fitted with standard taper joints. The tubes or bulbs were connected to stopcock adaptors, which in turn were connected to a reaction station on the vacuum line. The stopcock adaptor consisted of two standard taper joints of the proper size separated by a vacuum stopcock. The stopcock adaptor allowed the reaction vessel to be removed under vacuum from the vacuum line and transferred to the inert nitrogen atmosphere of a dry box without coming into contact with air. In the dry box, products were recovered and transferred to vials. The vials were capped, brought out of the dry box, and the caps sealed with paraffin. For reactants, which were sensitive to the air, the dry box was used to fill the reaction vessels; then the reaction vessels were evacuated on the vacuum line. When the extractor was put on or removed from the vacuum line, it was done under a dry nitrogen atmosphere.
6. **Infrared spectra**

All solid samples were run as solids in KBr pellets or in Nujol. Instruments used to obtain spectra were the Perkin-Elmer model 21 prism type recording spectrophotometer, the Perkin-Elmer 337 recording grating spectrophotometer with a range of 2.5 to 25 microns, and the Beckmann model IR 9 recording grating with KBr fore-prism spectrophotometer.

7. **Mass spectra**

A consolidated Engineering Model 21-620 mass spectrometer was used for the identification of volatile species.

8. **X-ray measurements**

X-rays were made using a Debye-Scherrer type camera of 11.46 cm. effective diameter with a North American Phillips X-ray instrument. Patterns were obtained using copper Kα radiation with an exposure time of 15 to 20 hours at 12 milliamperes and 32 kilovolts. Sensitive samples were sealed in 0.3 or 0.5 mm. X-ray capillaries under the inert nitrogen atmosphere of a dry box.

9. **Glass ware**

All glass ware, prior to use, was washed in alcoholic KOH solution, rinsed with distilled water, dried in an oven at 100°C. for several hours; and then taken to the vacuum system or to the dry box while the glass was still warm.
B. Chemicals

1. Diborane

Diborane was obtained from a commercial cylinder. After being purified by low temperature fractional distillation and stored at -196°C in the vacuum system, it was measured, volumetrically, as a gas at room temperature.

2. Ammonia

Ammonia was stored in the vacuum system over sodium at -78°C. to insure dryness of the ammonia. Ammonia used for molecular weight determinations was distilled into a 50 ml. weighing bulb, which was equipped with a vacuum stopcock, a glass wool filter, and contained lithium nitrate. The bulb of LiNO₃ was previously heated to 160°C. and pumped on for a week. The LiNO₃ bulb which contained the ammonia was kept at room temperature since a saturated solution of LiNO₃ in ammonia has a vapor pressure of approximately 45 cm. of Hg at room temperature. Desired amounts of ammonia were removed at room temperature and the ammonia's exact weight was obtained by the loss in weight of the LiNO₃ bulb.

3. Diammoniate of diborane

Diammoniate of diborane, $\text{BH}_2(\text{NH}_3)_2\text{BH}_4$, was prepared by the method of Parry and Shore (47) in a 25 x 300 mm. tube which was fitted with a 24/40 B joint. A measured
quantity of diborane was condensed in the tube above an excess of ammonia at -196°C. For reactions larger than three millimoles the ammonia was condensed above the diborane. By means of a slush bath of Skelly Solve F at -140°C., the chemicals were allowed to warm to -78°C. over a period of twelve hours, after which the excess ammonia was removed by sublimation.

4. **Diethyl ether, dimethyl ether, tetrahydrofuran, and Ansul 121**

These ethers were stored over LiAlH₄ in the vacuum system. The dry solvent was then distilled into the reaction vessel.

5. **Dimethyl sulfoxide**

Reagent grade dimethyl sulfoxide was obtained from the Crown Zellerbach Corporation. It was purified by heating it under dry nitrogen at 120°C. for an hour over one per cent by weight of NaOH or KOH. Then it was distilled at approximately 60°C. under a low pressure of dry nitrogen into a one-liter round bottom flask. The fore and afterruns were discarded. The dimethyl sulfoxide was capped under nitrogen until used.

6. **Sodium amide**

Sodium amide, obtained from Dr. K. Greenlee of the American Petroleum Institute Research Laboratories, was iron free since it was prepared from the reaction of sodium with an ammoniaisoprene solution.
7. **Sodium acetylide**

Sodium acetylide was prepared by the reaction of sodium with acetylene in liquid ammonia as described by Greenlee and Henne (48).

8. **Lithium amide**

Lithium amide was prepared by the reaction of ammonia with n-butyl lithium in hexane at -78°C. on the vacuum line. The n-butyl lithium, which was in hexane, was obtained from Foote Mineral Company. The excess ammonia, butane, and hexane were removed from the insoluble LiNH₂ by distillation.

9. **Lithium methylamide**

Lithium methylamide, LiMeNH₂, was prepared by the reaction of methylamine with n-butyl lithium in hexane at -78°C. on the vacuum line.

10. **Cyclotriborazane**

Cyclotriborazane, (BH₂NH₂)₃, was prepared through modification of the procedure of Dahl and Schaeffer (49). B₃H₅Cl₂N₃H₆ was formed by bubbling excess HCl into a solution containing 10 millimoles of borazine (50) in diethyl ether at -78°C. The ether was distilled away, leaving behind the solid hydrochloride adduct to which 35 millimoles of lithium borohydride was added. About 50 milliliters of anhydrous diethyl ether, containing 5 milliliters of glyme, was distilled into the flask. The system
was stirred at room temperature until diborane evolution ceased. Volatile materials were distilled away, leaving behind the dry ether-free residue, which was placed on a frit and washed with ice-cold water. The cyclotriborazane is insoluble in water, and unaffected by ice-cold water, provided ether is absent. A 90 per cent yield of crude cyclotriborazane was obtained and purified through extraction with liquid ammonia at -78°C.

C. Analytical Procedures

1. Solid analysis by acid hydrolysis

Sensitive solid samples were transferred in the dry box to a weighing pig, which was a 7/25 ® joint sealed at the bottom to a glass rod. The weighing pig was then capped with a 7/25 ® joint plug, brought out of the dry box, and weighed to 0.1 milligrams. The solid sample was transferred to a hydrolysis tube in the dry box and the weighing pig and cap reweighed to obtain the weight of the solid sample. The hydrolysis tube as illustrated in Figure 5 consisted of 10 millimeter Pyrex glass tubing through which the sample was introduced into the hydrolysis tube. With a rubber serum cap capping the 10 millimeter glass tubing, the hydrolysis tube was evacuated, and the 10 millimeter glass tubing sealed with a gas-oxygen torch. The sample was hydrolysed by distilling 6N hydrochloric acid into the hydrolysis tube at -196°C, sealing off the
Fig. 5.—Hydrolysis Tube
hydrolysis tube, and placing it in an oven at 100°C. for at least a day. The hydrolysis tube was then returned to the vacuum line, placed in liquid nitrogen, and opened by snapping off its break-off tip. The amount of hydrogen produced by the hydrolysis was measured in the Toepler system. The solution was diluted volumetrically, and aliquots were taken for boron and nitrogen analyses.

a. Nitrogen analysis.

Aliquots of the acidic solution were analyzed for nitrogen by standard Micro Kjeldahl methods. Titration was carried out using a Beckmann Model G pH meter. End points were determined from titration curves.

b. Boron analysis

Aliquots of the solution were analyzed for boron by titrating boric acid in the presence of Mannitol (51) with standard NaOH. The procedure involves the neutralization of the free acid with a base to a pH near 7. Mannitol is then added, which lowers the pH to approximately 3.5 by forming a complex with the boric acid. Titration with base is carried out, using the inflection point as the end point.

2. Solid analysis of boron and nitrogen by the method of Rittner and Culmo (52)

A weighed solid sample was introduced into a 30 milliliter Kjeldahl flask, which was fitted with a 24/40 # inner, O-ring joint. Several milliliters of concentrated sulfuric
acid, several milligrams of selenium, and several milligrams of a 3 to 1 mixture of cupric sulfate-potassium sulfate were added to the Kjeldahl flask. The flask was connected to a water-cooled condenser and heated to 370°C. by a Wood's metal bath for a day. The purpose of the condenser was to prevent any volatile boron compounds from escaping. The solution was cooled, diluted volumetrically, and aliquots were taken for boron and nitrogen analyses. The analyses were done as previously described, except for boron the free acid was neutralized to a pH of 7.1 to 7.3, mannitol added, and the acidic solution titrated with standard NaOH to the exact pH to which the solution had previously been neutralized.

D. Determination of the Cryoscopic Constant of Dimethyl Sulfoxide

Schwyzer and Siever (53) reported a cryoscopic constant of 4.99°C./molar for dimethyl sulfoxide. However, a redetermination of the cryoscopic constant of dimethyl sulfoxide in this laboratory yielded a value of 3.59°C./molar. The solutes used in this investigation were naphthalene, para dichlorobenzene, and urea.

A typical determination of the cryoscopic constant of dimethyl sulfoxide or of the molecular weight of a solute required use of the freezing point cell illustrated in Figure 3. With the Beckmann thermometer removed, the
cell was flushed with nitrogen and ten to fifteen milliliters of dimethyl sulfoxide was pippeted into the cell. The cell was again flushed with nitrogen and the Beckmann thermometer was inserted into the apparatus. Dimethyl sulfoxide (m.p. = 18.45°C.) was partially frozen by placing the cell in the double-walled vessel shown in Figure 2, which was cooled by ice water. Its freezing point was determined from a time-temperature warming curve by extrapolating to the point of inflection at which the first trace of solid in equilibrium with liquid appeared in the system (54). A warming curve was taken instead of its freezing point because dimethyl sulfoxide supercooled markedly. After the determination of the freezing point of dimethyl sulfoxide, the cell was opened and the sample of solute was added. Addition of the solute to the cell was accomplished by attaching the previously weighed sample vial to a glass rod by means of adhesive tape. The sample vial was then lowered into the cell and the sample dumped into the dimethyl sulfoxide. After this the cell was flushed with nitrogen and the Beckmann thermometer was reinserted. After stirring the solution, it was partially frozen and a time-temperature warming curve was obtained. Table 1 gives the results of the determination of the cryoscopic constant of dimethyl sulfoxide, and Figure 6 illustrates a typical warming curve of the solvent and of the solution.
Though dimethyl sulfoxide is highly hygroscopic, it can be capped in a flask under nitrogen for several months without its freezing point changing more than 0.001°C. Therefore, freezing point depressions can be studied by first adding the solute to the cell and then pipetting the dimethyl sulfoxide into the cell, the freezing point of which has been determined previously.

**TABLE 1**

**CRYOSCOPIC CONSTANT OF DIMETHYL SULFOXIDE**

<table>
<thead>
<tr>
<th>Solution</th>
<th>Sample</th>
<th>Wt. of Sample</th>
<th>°C.</th>
<th>°C./molar</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Naphthalene</td>
<td>461.3 mg.</td>
<td>0.855</td>
<td>3.56</td>
</tr>
<tr>
<td>2</td>
<td>Naphthalene</td>
<td>435.8 mg.</td>
<td>0.818</td>
<td>3.61</td>
</tr>
<tr>
<td>3</td>
<td>p-ClC₆H₄</td>
<td>451.3 mg.</td>
<td>0.726</td>
<td>3.55</td>
</tr>
<tr>
<td>4</td>
<td>p-ClC₆H₄</td>
<td>132.2 mg.</td>
<td>0.216</td>
<td>3.61</td>
</tr>
<tr>
<td>5</td>
<td>p-ClC₆H₄</td>
<td>203.1 mg.</td>
<td>0.333</td>
<td>3.62</td>
</tr>
<tr>
<td>6</td>
<td>Urea</td>
<td>83.0 mg.</td>
<td>0.329</td>
<td>3.57</td>
</tr>
</tbody>
</table>

*a* All solutions were of fifteen milliliter volume.

*b* Cryosopic constant, \( K = \frac{(\Delta T^\circ C.)(\text{ml. of Solvent})(\text{mol. wt. of solvent})}{(\text{wt. of solute in mg.})} \)
Fig. 6.—Typical Warming Curve of Solvent DMSO and of Solution
Typical warming curve of solvent DMSO

Typical warming curve of solution

1 inch = 0.1° C.
E. Reactions of Diammoniate of Diborane with Bases in Liquid Ammonia

Sodium dissolves readily in liquid ammonia without reducing the solvent to form sodium amide and hydrogen. Sodium amide forms only in the presence of a catalyst or at elevated temperatures (55). On the other hand, the ammonium ion, as in ammonium chloride, is reduced rapidly at -78°C.

\[
\text{NH}_4\text{Cl} + \text{Na} \xrightarrow{\text{NH}_3} \text{NH}_2 + \text{H}_2 + \text{NaCl}
\]

Sodium reacts with diammoniate of diborane in liquid ammonia at -78°C. Quaternization of nitrogen in the cation, \((\text{BH}_2(\text{NH}_3)_2)^+\), renders the protons on the ammonia susceptible to attack by a reducing agent or base due to the transfer of electron charge from the N-H bond. Therefore, not only was the sodium-diammoniate of diborane reaction re-examined, but other strong bases, namely sodium acetylide and sodium amide, were employed in the hope that they would abstract a proton from a coordinated ammonia on the cation, \(\text{BH}_2(\text{NH}_3)_2^+\), leading ultimately to aminoboranes or cycloborazanes.

1. Reactions
a. Diammoniate of diborane with sodium acetylide in liquid ammonia

The reaction of diammoniate of diborane with sodium acetylide in ammonia yielded acetylene, ammonia, sodium borohydride, cyclotriborazane and cyclopentaborazane.

\[
\text{NaC}==\text{CH} + \text{BH}_2(\text{NH}_3)_2\text{BH}_4 \xrightarrow{\text{NH}_3} \text{NaBH}_4 + \text{NH}_3
\]

\[
+\text{HC}==\text{CH} + (\text{BH}_2\text{NH}_2)_3,5
\]
A typical experiment involved the reaction of three millimoles of sodium acetylide with three millimoles of diammoniate of diborane in liquid ammonia at \(-78^\circ\text{C}\). Under the inert atmosphere of a dry box, a weighed quantity of \(\text{NaC}^\equiv\text{CH}\) was added to a 25 x 300 mm. tube which contained an equimolar quantity of \(\text{BH}_2(\text{NH}_3)_2\text{BH}_4\). The tube was fitted with a 24/40 \(\equiv\) joint. The reaction tube containing the 1:1 mole ratio of \(\text{NaC}^\equiv\text{CH}\) and \(\text{BH}_2(\text{NH}_3)_2\text{BH}_4\) was evacuated on the vacuum line and ten to fifteen milliliters of anhydrous ammonia was distilled into the tube and condensed at \(-78^\circ\text{C}\). The solution was stirred by a magnetic hopper stirrer. Reaction took place at \(-78^\circ\text{C}\). In most cases a precipitate was produced immediately; while in other runs the ammonia solution remained clear for approximately a day until a precipitate was noticeable. Both of the reactants, \(\text{NaC}^\equiv\text{CH}\) and \(\text{BH}_2(\text{NH}_3)_2\text{BH}_4\), are soluble in ammonia. Ammonia was removed by sublimation at \(-78^\circ\text{C}\), leaving behind a white, solid product, which proved to be sodium borohydride, cyclotriborazane, and cyclopentaborazane. Partial separation of the products was accomplished by extracting with ammonia, sodium borohydride and cyclotriborazane, from ammonia insoluble cyclopentaborazane. Cyclotriborazane (obtained in approximately 15 per cent yield) was then removed from the sodium borohydride by sublimation in \textit{vacuo} at 100–110°C. Separation of the aminoborane species from
sodium borohydride was also accomplished by treating the mixture with ice water; the aminoborane species being slightly soluble and stable in ice water.

That HC–CH was one of the products was demonstrated by distilling it into a sodium-ammonia solution, where it formed NaC–CH, which was identified from its X-ray powder diffraction pattern.

b. Diammoniate of diborane with sodium amide in liquid ammonia

The reaction of diammoniate of diborane with sodium amide in ammonia yielded sodium borohydride, ammonia, and cyclopentaborazane (large scale reactions yielded approximately one per cent cyclotriborazane (56).)

\[
\text{NaNH}_2 + \text{BH}_2(\text{NH}_3)_2\text{BH}_4 + \text{NH}_3 \rightarrow \text{NaBH}_4 + 2\text{NH}_3 + \frac{1}{5} (\text{BH}_2\text{NH}_2)_5
\]

A typical experiment involved the reaction of five millimoles of diammoniate of diborane with five millimoles of sodium amide in liquid ammonia at -78°C. Under the inert atmosphere of a dry box, a weighed quantity of NaNH\(_2\) was added to a 25 x 300 mm. tube which contained an equimolar quantity of BH\(_2(\text{NH}_3)_2\text{BH}_4\). The tube was fitted with a 24/40 B joint. The tube containing the reactants was evacuated and ten to fifteen milliliters of anhydrous ammonia was distilled and condensed in the tube at -78°C. The mixture was stirred magnetically by a magnetic stirring
bar, since sodium amide is insoluble in liquid ammonia. The distillation of ammonia was slow as the reaction generated about a mole of hydrogen for every ten moles of diammoniate of diborane present as illustrated in Table 2.

**TABLE 2**

**HYDROGEN GENERATED FROM THE REACTION OF SODIUM AMIDE WITH DIAMMONIATE OF DIBORANE**

<table>
<thead>
<tr>
<th>Millimoles of Diammoniate of Diborane Reacted</th>
<th>Millimoles of Hydrogen Generated</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.06</td>
<td>0.29</td>
</tr>
<tr>
<td>4.15</td>
<td>0.412</td>
</tr>
<tr>
<td>11.26</td>
<td>1.65</td>
</tr>
<tr>
<td>5.07</td>
<td>0.46</td>
</tr>
<tr>
<td>5.25</td>
<td>0.49</td>
</tr>
</tbody>
</table>

Reaction was followed at -78°C. by observing the disappearance of sodium amide which is insoluble in liquid ammonia. The solution usually became clear within a half hour. After approximately a day, the ammonia solution would become cloudy with the presence of a precipitate. The system was cooled to liquid nitrogen temperature and the hydrogen was measured by the Toepler system. Ammonia was then removed by sublimation at -78°C., leaving behind a white, solid product, which proved to be sodium boro-hydride and cyclopentaborazane, \((BH_2NH_2)_5\). Separation of
the products was accomplished by extracting with ammonia, sodium borohydride from ammonia insoluble cyclopentaborazane or by treating the mixture with ice water.

Attempts to trap monomeric BH₂NH₂ by forming an addition compound with a Lewis base, such as trimethylamine or trimethylphosphine, were unsuccessful. When the sodium amide-diammoniate of diborane reaction appeared complete as evidenced by the appearance of a clear ammonia solution, an excess of N(CH₃)₃ was condensed in the reaction tube. An X-ray diffraction pattern of the white solid remaining after removal of ammonia and trimethylamine gave "d" values for sodium borohydride and cyclopentaborazane. The same results were obtained when PMe₃ was used.

c. Diammoniate of diborane with sodium in liquid ammonia

The reaction of diammoniate of diborane with sodium in liquid ammonia yielded hydrogen, ammonia, sodium borohydride, and cyclopentaborazane according to the equation:

Na + BH₂(NH₃)₂BH₄ $\xrightarrow{NH₃}$ 1/2 H₂ + NH₃ + NaBH₄ + 1/5 (BH₂NH₂)₅

A typical experiment involved the reaction of five millimoles of diammoniate of diborane with five millimoles of sodium in liquid ammonia at -78°C. Under the inert atmosphere of a dry box, a weighed quantity of Na was added to a 25 x 300 mm. tube which contained an equimolar quantity
of $\text{BH}_2(\text{NH}_3)_2\text{BH}_4$. The tube was fitted with a 24/40 joint. The reaction tube containing a 1:1 mole ratio of Na and $\text{BH}_2(\text{NH}_3)_2\text{BH}_4$ was evacuated on the vacuum line and ten to fifteen milliliters of ammonia was condensed in the tube at $-196^\circ\text{C}$. The tube was then emersed in a Dry Ice-isopropyl alcohol bath at $-78^\circ\text{C}$. The resulting blue solution was stirred by a solenoid actuated stirrer at $-78^\circ\text{C}$. Within an hour hydrogen gas evolution ceased and the solution became colorless. The ammonia solution remained clear for approximately a day, after which a precipitate became noticeable. The system was cooled to $-196^\circ\text{C}$ and the hydrogen was measured by the Toepler system. See Table 3. Ammonia was removed by sublimation at $-78^\circ\text{C}$, leaving behind a white, solid product, which proved to be sodium borohydride and cyclopentaborazane as shown by their X-ray powder diffraction patterns.

2. Properties

a. Cyclotriborazane

Cyclotriborazane is a white solid, which is stable in moist air and water. An ammonia solution of $(\text{BH}_2\text{NH}_2)_3$ at room temperature showed no sign of a precipitate and an X-ray diffraction pattern of the solute remained unchanged. It is soluble in ammonia, diglyme, ether, dioxane, and methanol. Its solubility in water is low. It sublimes in vacuo at approximately 100°C. Complete hydrolysis is
is accomplished by treating it with 6N HCl at 100°C. for twelve hours.

**TABLE 3**

HYDROGEN GENERATED FROM THE REACTION OF SODIUM AND DIAMMONIATE OF DIBORANE

<table>
<thead>
<tr>
<th>Millimoles of Sodium</th>
<th>Millimoles of BH₂(NH₃)₂BH₄</th>
<th>Hydrogen Generated</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.49</td>
<td>4.57</td>
<td>2.11</td>
</tr>
<tr>
<td>5.43</td>
<td>5.53</td>
<td>2.48</td>
</tr>
<tr>
<td>19.1</td>
<td>19.1</td>
<td>-&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup>Not measured because of the large quantity of hydrogen evolved.

b. Cyclopentaborazane

Cyclopentaborazane is a white solid, which is stable in moist air and in liquid ammonia at room temperature. Complete hydrolysis is accomplished by treating it with 6N HCl at a temperature of 160°C. for a week. Solubility in ammonia and water is low, but it is soluble in dimethyl sulfoxide and dimethyl formamide. It is essentially insoluble in most organic solvents and does not react with methanol at room temperature to form methoxide derivatives.

3. X-ray powder diffraction patterns

The "d" spacings and corresponding relative intensities of the lines of the X-ray powder diffraction pattern
of cyclotriborazane and cyclopentaborazane are given in Tables 4 and 5, respectively, for purposes of identification.

**TABLE 4**

**X-RAY POWDER DIFFRACTION PATTERN OF CYCLOTribORAZANE**

<table>
<thead>
<tr>
<th>Intensity</th>
<th>(d(\text{Å}))</th>
<th>Intensity</th>
<th>(d(\text{Å}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>s</td>
<td>6.14</td>
<td>vw</td>
<td>2.68</td>
</tr>
<tr>
<td>s</td>
<td>5.57</td>
<td>w</td>
<td>2.55</td>
</tr>
<tr>
<td>w</td>
<td>4.42</td>
<td>w</td>
<td>2.335</td>
</tr>
<tr>
<td>vs</td>
<td>3.90</td>
<td>w</td>
<td>2.209</td>
</tr>
<tr>
<td>w</td>
<td>3.05</td>
<td>vw</td>
<td>2.146</td>
</tr>
<tr>
<td>vw</td>
<td>2.80</td>
<td>vvw</td>
<td>1.795</td>
</tr>
</tbody>
</table>

Intensities:  v = very; w = weak; m = medium; s = strong.

\((\text{Cu-K}_\alpha) = 1.5418 \text{ Å} .\)

**TABLE 5**

**X-RAY POWDER DIFFRACTION PATTERN OF CYCLOPENTABORAZANE**

<table>
<thead>
<tr>
<th>Intensity</th>
<th>(d(\text{Å}))</th>
<th>Intensity</th>
<th>(d(\text{Å}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>m</td>
<td>4.39</td>
<td>w</td>
<td>1.895</td>
</tr>
<tr>
<td>vs</td>
<td>3.80</td>
<td>vw</td>
<td>1.668</td>
</tr>
<tr>
<td>w</td>
<td>2.87</td>
<td>vw</td>
<td>1.538</td>
</tr>
<tr>
<td>m</td>
<td>2.188</td>
<td>vw</td>
<td>1.433</td>
</tr>
<tr>
<td>vw</td>
<td>2.108</td>
<td>vw</td>
<td>1.258</td>
</tr>
</tbody>
</table>

Intensities:  v = very; w = weak; m = medium; s = strong.

\((\text{Cu-K}_\alpha) = 1.5418 \text{ Å} .\)
4. Molecular weights
   a. Cyclotriborazane

   The molecular weight of \((\text{BE}_{3}\text{NH})_3\) was determined cryoscopically in liquid ammonia. Because of the low yields of cyclotriborazane obtained in the sodium acetylide-diammoniate of diborane reaction, it was prepared through modification of the procedure of Dahl and Schaeffer (49). See the chemical section. The results of the molecular weight study of cyclotriborazane are given in Table 6. They are in good agreement with the theoretical value of 86.5.

   **TABLE 6**

   **APPARENT MOLECULAR WEIGHT OF CYCLOTRIBORAZANE IN LIQUID AMMONIA**

<table>
<thead>
<tr>
<th>Solution</th>
<th>Molality (based on ((\text{BE}_{3}\text{NH})_3))</th>
<th>Mol. Wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.140</td>
<td>83±1</td>
</tr>
<tr>
<td>2</td>
<td>0.235</td>
<td>84±2</td>
</tr>
</tbody>
</table>

   Solution 1, Table 6, was prepared from cyclotriborazane which had been allowed to stand at room temperature under a dry nitrogen atmosphere for a period of one month. Solution 2, Table 6, was prepared from a fresh sample of cyclotriborazane.
As a test of the stability of this compound in liquid ammonia, freezing point measurements were made on the freshly prepared ammonia solution which were maintained at -78°C, and on the same solutions after they had been allowed to stand for about 30 hours at -45°C. The molecular weights agreed, for each solution, within the precision cited above. Also the X-ray powder diffraction pattern of cyclotriborazane remained unchanged after each molecular weight determination.

b. Cyclopentaborazane

The molecular weight of \((\text{BH}_2\text{NH}_2)_5\) was determined cryoscopically in dimethyl sulfoxide. The cryoscopic technique using dimethyl sulfoxide is described in part D of this section. The results of the molecular weight study are given in Table 7, and are in excellent agreement with the formula, \((\text{BH}_2\text{NH}_2)_5\), which has a molecular weight of 144.3.

5. Infrared spectra
a. Cyclotriborazane

The spectrum of cyclotriborazane, \((\text{BH}_2\text{NH}_2)_3\), from infrared spectrometry, using the KBr pellet technique, is shown in Figure 7. The absorption bands are given in Table 8. The broad band at 2380-2300 cm\(^{-1}\) is assigned to the symmetric and asymmetric BH\(_2\) stretching frequency, which is sufficiently low to be indicative of quaternary boron (57).
For example, in diborane the asymmetric and symmetric BH$_2$ stretching frequencies are 2614 and 2522 cm.$^{-1}$, respectively (58) and in sodium borohydride the BH stretching frequencies of the quaternary boron are a strong combination band at 2250-2400 cm.$^{-1}$ (59).

### TABLE 7

APPARENT MOLECULAR WEIGHT OF CYCLOPENTABORAZANE IN DIMETHYL SULFOXIDE

<table>
<thead>
<tr>
<th>Solution</th>
<th>Molecular Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>148.3</td>
</tr>
<tr>
<td>2</td>
<td>141.8</td>
</tr>
<tr>
<td>3</td>
<td>147.2</td>
</tr>
<tr>
<td>4</td>
<td>139.5</td>
</tr>
<tr>
<td>5</td>
<td>147.1</td>
</tr>
</tbody>
</table>

There is no evidence for hydrogen-bridged borons since in diborane the BH stretching frequency for the hydrogen-bridged boron is 1604 cm.$^{-1}$ (58). The absorption bands of 3312 and 3264 cm.$^{-1}$ are assigned to asymmetric and symmetric NH$_2$ stretching frequency, respectively, and the absorption bands of 1588 and 1569 cm.$^{-1}$ are assigned to the NH$_2$ deformation doublet.

b. Cyclopentaborazane

A typical infrared spectrum of a KBr pellet of solid (BH$_2$NH$_2$)$_5$ is shown in Figure 8, and a detailed spectrum of
Fig. 7.---Infrared Spectrum of \( (\text{BH}_2\text{NH}_2)_3 \)
absorption bands is given in Table 9. The spectrum of
(BH₂NH₂)₅ is very similar to the spectrum of (BH₂NH₂)₃ with
a BH₂ stretching frequency of 2420-2300 cm⁻¹ and an asym­
metric and symmetric NH₂ stretching frequency of 3301 and
3250 cm⁻¹, respectively. The NH₂ deformation doublet
appears as only a singlet of 1571 cm⁻¹, but there does
appear to be a very small shoulder at 1580 cm⁻¹. The one
major difference between cyclotriborazane and cyclopenta­
borazane is the presence of a medium absorption at 1412 cm⁻¹
in the (BH₂NH₂)₅ spectrum, which is assigned to the B-N
stretching frequency (27,29).

TABLE 8
INFRARED SPECTRUM OF (BH₂NH₂)₃

<table>
<thead>
<tr>
<th>Freq. (cm⁻¹)</th>
<th>Intensity</th>
<th>Freq. (cm⁻¹)</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>3312</td>
<td>s, sp</td>
<td>1140</td>
<td>s, sp</td>
</tr>
<tr>
<td>3264</td>
<td>s, sp</td>
<td>1067</td>
<td>m, sp</td>
</tr>
<tr>
<td>2380-2300</td>
<td>s, br</td>
<td>1052</td>
<td>m, sp</td>
</tr>
<tr>
<td>1588</td>
<td>m, sp</td>
<td>1005</td>
<td>w, sp</td>
</tr>
<tr>
<td>1569</td>
<td>m, sp</td>
<td>893</td>
<td>w, sp</td>
</tr>
<tr>
<td>1238</td>
<td>s, sp</td>
<td>827</td>
<td>w, sp</td>
</tr>
<tr>
<td>1200</td>
<td>s, sp</td>
<td>690</td>
<td>w, sp</td>
</tr>
</tbody>
</table>

Intensities:  s = strong;  m = medium;  w = weak;  s =
sharp;  br = broad;  sh = shoulder.
Fig. 8.—Infrared Spectrum of $\text{(BH}_2\text{NH}_2)_5$
Infrared spectrum of (BH$_2$NH$_2$)$_5$
TABLE 9
INFRARED SPECTRUM OF \((BH_{2}NH_{2})_{5}\)

<table>
<thead>
<tr>
<th>Freq. (cm(^{-1}))</th>
<th>Intensity</th>
<th>Freq. (cm(^{-1}))</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>3301</td>
<td>s, sp</td>
<td>1087</td>
<td>m, sp</td>
</tr>
<tr>
<td>3250</td>
<td>s, sp</td>
<td>1062</td>
<td>m, sp</td>
</tr>
<tr>
<td>2420-2300</td>
<td>s, br</td>
<td>973</td>
<td>w</td>
</tr>
<tr>
<td>1571</td>
<td>m, sp</td>
<td>845</td>
<td>w</td>
</tr>
<tr>
<td>1412</td>
<td>m</td>
<td>650</td>
<td>w</td>
</tr>
<tr>
<td>1205</td>
<td>s</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Intensities: s = strong; m = medium; w = weak; sp = sharp; br = broad; sh = shoulder.

6. Analyses
a. Cyclotriborazane

The analysis for \((BH_{2}NH_{2})_{3}\) is given in Table 10. The sample used is one that had been recovered after a molecular weight determination in liquid ammonia.

TABLE 10
ANALYSIS OF \((BH_{2}NH_{2})_{3}\)

<table>
<thead>
<tr>
<th></th>
<th>%B</th>
<th>%N</th>
<th>%H (hydridic)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Found</td>
<td>37.9</td>
<td>49.8</td>
<td>7.01</td>
</tr>
<tr>
<td>Calcd.</td>
<td>37.6</td>
<td>48.6</td>
<td>7.00</td>
</tr>
</tbody>
</table>
b. Cyclopentaborazane

While the complete hydrolysis of $(BH_2NH_2)_3$ to hydrogen, boric acid, and ammonium chloride by 6N HCl at 100°C. required only a day, the $(BH_2NH_2)_5$ proved to be more resistant to acid hydrolysis. Table 11 shows the results of the hydrolysis of $(BH_2NH_2)_5$ with 6 N HCl at 100°C., in which only about 80 per cent of the material was hydrolyzed.

**TABLE 11**

ANALYSIS OF $(BH_2NH_2)_5$ IN 6N HCl AT 100°C.

<table>
<thead>
<tr>
<th>Days at 100°C</th>
<th>Mmoles of $BH_2NH_2)_5$ (mmoles)</th>
<th>$H^-$ (mmoles)</th>
<th>B (mmoles)</th>
<th>N (mmoles)</th>
<th>H:B:N</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 1/2</td>
<td>1.334</td>
<td>2.26</td>
<td>1.18</td>
<td>1.07</td>
<td>1.92:1.00:0.91</td>
</tr>
<tr>
<td>2 1/2</td>
<td>1.341</td>
<td>2.07</td>
<td>1.069</td>
<td>1.055</td>
<td>1.94:1.00:0.99</td>
</tr>
<tr>
<td>3 1/2</td>
<td>1.726</td>
<td>2.84</td>
<td>1.41</td>
<td>1.43</td>
<td>2.01:1.00:1.01</td>
</tr>
</tbody>
</table>

Complete acid hydrolysis of the $(BH_2NH_2)_5$ was accomplished by heating the hydrolysis tube for a week at 160°C. Table 12 gives the results of the analysis, which shows the $(BH_2NH_2)_5$ to be around 97 per cent pure.
TABLE 12
ANALYSIS OF \((\text{BH}_2\text{NH}_2)_5\)

<table>
<thead>
<tr>
<th>Sample</th>
<th>% Boron</th>
<th>% Nitrogen</th>
<th>% Hydridic Hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>34.5</td>
<td>47.1</td>
<td>6.75</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>45.8</td>
<td>6.68</td>
</tr>
<tr>
<td>3</td>
<td>35.6</td>
<td>47.0</td>
<td>6.72</td>
</tr>
<tr>
<td>4</td>
<td>36.5</td>
<td>47.0</td>
<td>6.82</td>
</tr>
</tbody>
</table>

The theoretical percentages are 6.985 for hydridic hydrogen, 37.49 for boron, and 48.54 for nitrogen.

F. Reaction of Lithium Amide with Diborane in Diethyl Ether

Since the reaction of diammoniate of diborane with bases yielded cyclic forms of aminoborane, a re-examination of Schaeffer and Basile's work, in which aminoborane was formed from the reaction of lithium amide with diborane in diethyl ether, was undertaken.

1. Reaction of lithium amide with diborane in ether

The reaction of diborane with lithium amide in diethyl ether yielded lithium borohydride and aminoborane. The aminoborane was found to be an open chain polymer with an average length of 3 1/2 to 4 1/2 units.

\[
\text{LiNH}_2 + \text{B}_2\text{H}_6 \xrightarrow{\text{Et}_2\text{O}} \text{LiBH}_4 + (\text{BH}_2\text{NH}_2)_3.5-4.5
\]
The reaction was run in two ways: (1) in a 100 ml. bulb, which was attached to a vacuum line extractor to facilitate separation of the products, (2) in a previously weighed 100 ml. bulb to study the yield of the reaction.

a. Reaction using an extractor

A typical experiment involved the reaction of nine millimoles of lithium amide with an excess of diborane (twelve-thirteen millimoles). Under the inert atmosphere of a dry box, a weighed quantity of lithium amide was added to a 100 ml. bulb which was fitted with a 24/40 $\phi$ joint. The bulb was connected to the top of the vacuum line extractor and an identical bulb was connected to the bottom of the extractor (see Figure 4). After the extractor had been evacuated on the vacuum line, approximately forty-five milliliters of diethyl ether was condensed on the lithium amide at $-78^\circ$C. The mixture was then frozen to $-196^\circ$C, and diborane was condensed above the solid mixture. The reaction bulb was immersed in a beaker containing either a cold bath of Skelly Solve F or one of Dry Ice-isopropyl alcohol. The use of a beaker to contain the cold bath, allowed the reaction mixture to warm to $0^\circ$C. over a period of one to two hours. The reaction system was stirred constantly with a teflon magnetic stirring bar, since lithium amide is insoluble in diethyl ether and diborane is partially soluble in diethyl ether.
Separation of the products, lithium borohydride and aminoborane, was accomplished by inverting the extractor, since the aminoborane was insoluble in diethyl ether and lithium borohydride was ether soluble.

After cooling the ether solution to -196°C., the trace amounts of hydrogen evolved in the course of the reaction were measured in the Toepler system. Unreacted diborane was distilled from the reaction at -78°C., passed through a trap at -140°C., and was recovered in a trap at -196°C. A period of at least one and one-half hours was required for the fractional distillation of the diborane.

Ether insoluble aminoborane was washed three or four times with the diethyl ether used in the reaction. The ether was filtered at approximately 0°C. to remove all traces of lithium borohydride from the aminoborane. During the filtration process, the ether-aminoborane mixture was stirred with the teflon encased magnetic stirrer which had fallen on the frit when the extractor was inverted. Ether was distilled from the filtrate leaving behind lithium borohydride. The solid products, lithium borohydride and aminoborane, were dried at room temperature on the vacuum system for a day or two. Then the extractor was removed from the vacuum line under nitrogen and under the inert nitrogen atmosphere of a dry box, the separated products were recovered.
Quantities of LiNH₂ and B₂H₆ used, the excess B₂H₆ recovered, and the hydrogen evolved for different runs are given in Table 13. Table 13 shows that one mole of diborane reacts with one mole of lithium amide and that only a small trace of hydrogen is produced.

**TABLE 13**

**REACTIONS USING THE EXTRACTOR**

<table>
<thead>
<tr>
<th>Run</th>
<th>Milligrams of LiNH₂</th>
<th>Millimoles of B₂H₆</th>
<th>Exp. B₂H₆ Recovered</th>
<th>Theor. B₂H₆ Recovered</th>
<th>Mmoles H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>215</td>
<td>12.25</td>
<td>3.04</td>
<td>2.89</td>
<td>0.091</td>
</tr>
<tr>
<td>2</td>
<td>210</td>
<td>11.87</td>
<td>2.67</td>
<td>2.72</td>
<td>0.135</td>
</tr>
<tr>
<td>3</td>
<td>120</td>
<td>8.03</td>
<td>2.82</td>
<td>2.81</td>
<td>0.055</td>
</tr>
<tr>
<td>4</td>
<td>200</td>
<td>11.97</td>
<td>3.45</td>
<td>3.26</td>
<td>0.134</td>
</tr>
<tr>
<td>5</td>
<td>200</td>
<td>11.56</td>
<td>2.57</td>
<td>2.85</td>
<td>0.118</td>
</tr>
</tbody>
</table>

*The theoretical diborane that should be recovered from a reaction of only one mole of diborane with one mole of lithium amide.*

b. Yield study

A study was undertaken to investigate the yield of lithium borohydride from the reaction of lithium amide with diborane in diethyl ether. A typical experiment involved the reaction of nine millimoles of lithium amide with an excess of diborane (twelve-thirteen millimoles). Under the inert atmosphere of a dry box, a weighed quantity of lithium
amide was added to a 100 ml. bulb which was fitted with a 24/40 joint. The weight of the lithium amide was accurate to 0.1 milligrams since it was weighed in a capped glass vial under dry nitrogen on an analytical balance. Previously recorded was the total weight of the 100 ml. bulb, teflon encased stirring bar which was to be used to stir the reaction, and a rubber serum cap which was to be used to cap the bulb. By means of a stopcock adaptor, the bulb was evacuated and approximately forty-five milliliters of diethyl ether was distilled and condensed into the bulb at -78°C. The mixture was then frozen to -196°C., and diborane was condensed above the solid mixture. The reaction bulb was immersed in a beaker containing either a cold bath of Skelly Solve F or one of Dry Ice-isopropyl alcohol. The use of a beaker for the cold bath, allowed the reaction mixture to warm to 0°C. over a period of one to two hours. The reaction system was stirred constantly with a teflon magnetic stirring bar, since lithium amide is insoluble in diethyl ether and diborane is partially soluble in diethyl ether.

After cooling the ether solution to -196°C., the trace amounts of hydrogen evolved in the course of the reaction were measured in the Toepler system. Unreacted diborane was distilled from the reaction at -78°C., passed through a trap at -140°C., and recovered in a trap at -196°C. A period of at least one and one half hours was
required for the fractional distillation of the diborane. Ether was removed by distillation and the remaining white, solid product was dried in the vacuum system for one day.

Under the inert nitrogen atmosphere of a dry box, the stopcock adaptor was removed and the 100 ml. bulb was capped with the rubber serum cap. The bulb and contents were then weighed on an analytical balance. The results of the yield study experiment reaction are given in Table 14, which shows, as Table 13 did, that only one mole of diborane reacts with one mole of lithium amide to form aminoborane and lithium borohydride.

Separation of the products, lithium borohydride and aminoborane, was accomplished by an ether extraction on the vacuum line or by an ether extraction under the inert nitrogen atmosphere of a dry box.

2. Properties of ether insoluble aminoborane

Aminoborane is a white, amorphous solid which does not sublime. Heating it in vacuum causes decomposition rather than sublimation. It is sensitive to moist air and is easily protolized by methanol and water. It does not react with diborane as shown in Tables 13 and 14. It can not be isolated free of ether. Analyses gives approximately six per cent carbon content. When 150 milligrams of the substance was heated at 65°C. in vacuo for three hours, 0.144 millimoles of hydrogen and 0.130 millimoles of diethyl
<table>
<thead>
<tr>
<th>Run</th>
<th>Mmoles LiNH₂</th>
<th>Mmoles B₂H₆</th>
<th>Exp. B₂H₆ Recovered</th>
<th>Theor. B₂H₆ Recovered</th>
<th>Mmoles H₂</th>
<th>Exp. Yield (mg.)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Theor. Yield (mg.)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.391</td>
<td>10.12</td>
<td>1.67</td>
<td>1.73</td>
<td>-</td>
<td>414</td>
<td>425</td>
</tr>
<tr>
<td>2</td>
<td>8.918</td>
<td>11.04</td>
<td>2.2</td>
<td>2.13</td>
<td>0.079</td>
<td>435</td>
<td>452</td>
</tr>
<tr>
<td>3</td>
<td>8.46</td>
<td>10.95</td>
<td>2.48</td>
<td>2.49</td>
<td>0.108</td>
<td>410</td>
<td>429</td>
</tr>
<tr>
<td>4</td>
<td>8.79</td>
<td>11.42</td>
<td>3.44</td>
<td>2.63</td>
<td>0.231</td>
<td>388</td>
<td>445</td>
</tr>
<tr>
<td>5</td>
<td>8.24</td>
<td>11.45</td>
<td>3.28</td>
<td>3.21</td>
<td>0.059</td>
<td>390</td>
<td>418</td>
</tr>
<tr>
<td>6</td>
<td>9.25</td>
<td>12.72</td>
<td>3.26</td>
<td>3.47</td>
<td>-</td>
<td>440</td>
<td>469</td>
</tr>
<tr>
<td>7</td>
<td>16.36</td>
<td>22.49</td>
<td>5.60</td>
<td>6.12</td>
<td>-</td>
<td>770</td>
<td>829</td>
</tr>
</tbody>
</table>

<sup>a</sup>Weight of the products, lithium borohydride and aminoborane.
ether were evolved. The gases were identified by mass spectrometry.

The substance is readily soluble in liquid ammonia and dimethyl sulfoxide. It does not form a crystalline solid when recovered from these solvents. Moreover, it is essentially insoluble in common organic solvents.

3. Protolysis of aminoborane with methanol

Aminoborane can easily be protolized by methanol. Under the inert nitrogen atmosphere of a dry box, a weighed quantity of aminoborane was added to a reaction tube which was fitted with a 24/40 joint. The tube was evacuated and approximately five milliliters of methanol was distilled and condensed in the tube at -196°C. The mixture was warmed to room temperature and stirred by a teflon encased magnetic stirring bar. In approximately two hours hydrogen evolution ceased. The clear methanol solution was then frozen to -196°C. and the hydrogen measured by the Toepler system. Table 15 gives the results of these experiments.

For more accurate data concerning the protolysis of aminoborane by methanol, the frozen mixture of aminoborane and methanol was warmed quickly from -196°C. to 0°C. by immersing the reaction tube in a Dewar of ice water. The results of this experiment are given in Table 16. Figure 9 shows a plot of the per cent available hydrogen per $\text{BH}_2\text{NH}_2$ versus the time.
TABLE 15
RESULTS OF PROTOLYSIS OF AMINOBORANE WITH METHANOL

<table>
<thead>
<tr>
<th>Run</th>
<th>Weight of Aminoborane&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Time&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Mmoles of Hydrogen</th>
<th>Per Cent H&lt;sub&gt;2&lt;/sub&gt;/Available H&lt;sub&gt;2&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>24.2 mg.</td>
<td>2 hr.</td>
<td>0.546</td>
<td>32.5</td>
</tr>
<tr>
<td>2</td>
<td>22.4 mg.</td>
<td>2 hr.</td>
<td>0.538</td>
<td>34.7</td>
</tr>
<tr>
<td>3</td>
<td>66.6 mg.</td>
<td>2 hr.</td>
<td>1.595</td>
<td>34.6</td>
</tr>
<tr>
<td>4</td>
<td>200.8 mg.</td>
<td>4 hr.</td>
<td>4.218</td>
<td>30.3</td>
</tr>
<tr>
<td>5</td>
<td>31.3 mg.</td>
<td>2 hr.</td>
<td>0.559</td>
<td>25.8</td>
</tr>
</tbody>
</table>

<sup>a</sup>It must be noted that the weight given is not the true weight of the aminoborane because about ten per cent of it is absorbed diethyl ether.

<sup>b</sup>The times given are relative, for the time includes that of warming from -196°C. to room temperature.

While cyclotriborazane and cyclopentaborazane are stable towards methanol, the aminoborane isolated from the ether reaction is easily protolized by methanol as indicated in both Tables 15 and 16. Chemically, this indicates that the aminoborane is a chain-like structure with a terminal BH<sub>2</sub> group, which is not quaternary. Figure 9 indicates that about 30 per cent of the available hydridic hydrogen per BH<sub>2</sub>NH<sub>2</sub> is rapidly attacked, which indicates an average chain length of about 3 1/2 BH<sub>2</sub>NH<sub>2</sub> units. For example, if the aminoborane contained four BH<sub>2</sub>NH<sub>2</sub> units
then the rapid protolysis by methanol could be represented by the following equation:

\[
\begin{align*}
\text{H}_2\text{B-(NH}_2\text{BH}_2)_3\text{NH}_2 + 2\text{MeOH} & \rightarrow \text{MeO-} \text{B-(NH}_2\text{BH}_2)_3\text{NH}_2 + \text{H}_2 \\
\end{align*}
\]

TABLE 16

<table>
<thead>
<tr>
<th>Run</th>
<th>Weight of Aminoborane$^a$</th>
<th>Total Time at 0°C.</th>
<th>Mmole of Hydrogen</th>
<th>Per Cent H$_2$/Available H$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>42.7 mg.</td>
<td>1.42 hr.</td>
<td>0.777</td>
<td>26.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.97 hr.</td>
<td>0.861</td>
<td>29.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>17.27 hr.</td>
<td>0.935</td>
<td>31.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20.77 hr.</td>
<td>0.955</td>
<td>32.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>137.27 hr.</td>
<td>1.103</td>
<td>37.8</td>
</tr>
<tr>
<td>2</td>
<td>25.2 mg. $^b$</td>
<td>0.80 hr.</td>
<td>0.512</td>
<td>29.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.13 hr.</td>
<td>0.537</td>
<td>30.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>16.3 hr.</td>
<td>0.554</td>
<td>31.7</td>
</tr>
</tbody>
</table>

$^a$It must be noted that the weight given is not the true weight of aminoborane because it is not free of ether.

$^b$The aminoborane had been heated at 65°C. for three days to remove any ether. Only 0.083 millimoles of hydrogen had been evolved in the course of the three days.
Fig. 9.—Protolysis of Aminoborane by Methanol at 0°C.
Protolysis of aminoborane by methanol at 0°C.
4. Molecular weights

a. Molecular weight in dimethyl sulfoxide

The molecular weight of aminoborane from the reaction of lithium amide with diborane in diethyl ether was studied cryoscopically in dimethyl sulfoxide. The cryoscopic technique, using dimethyl sulfoxide, is described in part D of this section. The results of the molecular weight study are given in Table 17. Several degrees of association are: \((\text{BH}_2\text{NH}_2)_3 = 86.6\), \((\text{BH}_2\text{NH}_2)_4 = 115.4\), and \((\text{BH}_2\text{NH}_2)_5 = 144.3\).

**TABLE 17**

**CRYOSCOPIC STUDY OF AMINOBORANE IN DIMETHYL SULFOXIDE**

<table>
<thead>
<tr>
<th>Solution</th>
<th>Weight of Aminoborane</th>
<th>Milliliters of DMSO</th>
<th>T (°C.)</th>
<th>Mol. Wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>134.3 mg.</td>
<td>15.00</td>
<td>0.289</td>
<td>111</td>
</tr>
<tr>
<td>2</td>
<td>146.7 mg.</td>
<td>15.00</td>
<td>0.337</td>
<td>105</td>
</tr>
<tr>
<td>3</td>
<td>60.0 mg.(^a)</td>
<td>15.00</td>
<td>0.140</td>
<td>103</td>
</tr>
<tr>
<td>4</td>
<td>97.8 mg.(^a)</td>
<td>15.00</td>
<td>0.277</td>
<td>85</td>
</tr>
<tr>
<td>5</td>
<td>117.6 mg.</td>
<td>15.00</td>
<td>0.180</td>
<td>155</td>
</tr>
<tr>
<td>6</td>
<td>75.6 mg.</td>
<td>14.63</td>
<td>0.122</td>
<td>152</td>
</tr>
<tr>
<td>7</td>
<td>92.5 mg.</td>
<td>9.13</td>
<td>0.362</td>
<td>101</td>
</tr>
</tbody>
</table>

\(^a\)These samples had been heated for two hours at 80°C. under vacuum and had been purified by an ammonia extraction.
The molecular weights obtained in Table 17 are not consistent but range from \((\text{BH}_2\text{NH}_2)_3\) to \((\text{BH}_2\text{NH}_2)_5\). The inconsistencies of the molecular weights in Table 17 indicate that the aminoborane is not homogeneous but a mixture of different degrees of association of an average of about four units. This is consistent with the protolysis experiments.

b. Molecular weight in liquid ammonia

The molecular weight of aminoborane in liquid ammonia was determined cryoscopically. Results are given in Table 18. The runs for the cooling curves of the ammonia

<table>
<thead>
<tr>
<th>TABLE 18</th>
</tr>
</thead>
<tbody>
<tr>
<td>CRYOSCOPIC STUDY OF AMINOBORANE IN LIQUID AMMONIA</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Solu-</th>
<th>Weight of Aminoborane</th>
<th>F.P. of (\text{NH}_3) (ohms)</th>
<th>F.P. of Soln. (ohms)</th>
<th>Mol. Wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>127.6 mg. 17.4789</td>
<td>17.4697</td>
<td>133.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>17.4789</td>
<td>17.4693</td>
<td>127.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>17.4791</td>
<td>17.4700</td>
<td>137.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>17.4790</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Av. 17.4790</td>
<td>Av. 17.4665</td>
<td>Av. 132.6</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>143.2 mg. 17.4778</td>
<td>17.4667</td>
<td>124.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>17.4779</td>
<td>17.4658</td>
<td>114.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Av. 17.4779</td>
<td>17.4665</td>
<td>121.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>17.4660</td>
<td>116.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Av. 119.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
solution were made over a period of two to three days and in Table 18 they are given in the order the run was made.

5. **X-ray powder diffraction patterns**

X-ray diffraction patterns were made of the ether soluble lithium borohydride and the ether insoluble aminoborane at 32 kilovolts and 12 milliamperes using a Cu-Kα of 1.5418 Å source for 18 hours. The ether insoluble aminoborane was amorphous and also amorphous after it had been dissolved in ammonia and dimethyl sulfoxide. The "d" spacings of the lithium borohydride are given in Table 19 along with the "d" spacings obtained by Meibohm (60).

6. **Infrared spectrum**

Figure 10 shows a typical infrared spectrum of aminoborane isolated from the ether reaction. Table 20 gives a detailed spectrum of the absorption bands. Though the KBr pellet was prepared in the dry box except for pressing the pellet, there was always a large, broad water absorption around 2.9 microns. The appearance of this band is expected because of the hygroscopic nature of aminoborane. The spectrum is not as sharp as those of cyclotriborazane and cyclopentaborazane. The NH₂ stretching doublet is present as a single, broad absorption of 3320-3220 cm⁻¹. The symmetric and asymmetric BH₂ stretching frequencies are a broad absorption at 2380-2280 cm⁻¹, which is identical to that of cyclotriborazane and cyclopentaborazane. The
The NH$_2$ deformation absorption is at 1575 cm.$^{-1}$ and the B-N absorption is at 1405 cm.$^{-1}$.

### Table 19

**X-Ray Powder Diffraction Pattern of Lithium Borohydride**

<table>
<thead>
<tr>
<th>Lithium Borohydride from Ether Reaction</th>
<th>Intensity</th>
<th>d(Å)</th>
<th>Meibohm's Pattern$^a$</th>
<th>Intensity</th>
<th>d(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>m</td>
<td>4.95</td>
<td></td>
<td>ms</td>
<td>4.955</td>
<td></td>
</tr>
<tr>
<td>m</td>
<td>3.72</td>
<td></td>
<td>vs</td>
<td>3.712</td>
<td></td>
</tr>
<tr>
<td>m</td>
<td>3.59</td>
<td></td>
<td>m</td>
<td>3.572</td>
<td></td>
</tr>
<tr>
<td>w+</td>
<td>3.41</td>
<td></td>
<td>mw</td>
<td>3.416</td>
<td></td>
</tr>
<tr>
<td>m</td>
<td>3.31</td>
<td></td>
<td>vs</td>
<td>3.294</td>
<td></td>
</tr>
<tr>
<td>w</td>
<td>3.08</td>
<td></td>
<td>m</td>
<td>3.082</td>
<td></td>
</tr>
<tr>
<td>vw</td>
<td>2.80</td>
<td></td>
<td>mw</td>
<td>2.781</td>
<td></td>
</tr>
<tr>
<td>w</td>
<td>2.58</td>
<td></td>
<td>w</td>
<td>2.591</td>
<td></td>
</tr>
<tr>
<td>w</td>
<td>2.54</td>
<td></td>
<td>w</td>
<td>2.520</td>
<td></td>
</tr>
<tr>
<td>w</td>
<td>2.48</td>
<td></td>
<td>w</td>
<td>2.461</td>
<td></td>
</tr>
<tr>
<td>w</td>
<td>2.26</td>
<td></td>
<td>w</td>
<td>2.270</td>
<td></td>
</tr>
<tr>
<td>w</td>
<td>2.22</td>
<td></td>
<td>ms</td>
<td>2.215</td>
<td></td>
</tr>
<tr>
<td>vm</td>
<td>2.025</td>
<td></td>
<td>s</td>
<td>2.021</td>
<td></td>
</tr>
<tr>
<td>w</td>
<td>1.793</td>
<td></td>
<td>ms</td>
<td>1.792</td>
<td></td>
</tr>
<tr>
<td>w</td>
<td>1.762</td>
<td></td>
<td>m</td>
<td>1.756</td>
<td></td>
</tr>
<tr>
<td>w</td>
<td>1.585</td>
<td></td>
<td>ms</td>
<td>1.580</td>
<td></td>
</tr>
</tbody>
</table>

Intensities: v = very; w = weak; m = medium; s = strong.

$^a$There were also an additional twenty-seven lines whose intensities were very weak.

7. **Reactions of aminoborane**

Lithium aluminum hydride reacts rapidly with ammonia in diethyl ether at low temperatures to yield H$_2$ and LiA$_2$H$_3$NH$_2$ (61). Aminoborane does not react rapidly with lithium aluminum hydride in diethyl ether. Under the inert
Fig. 10.--Infrared Spectrum of Aminoborane from Ether Reaction
Infrared spectrum of Amino Borane from ether reaction
nitrogen atmosphere of a dry box, approximately one millimole of $\text{BH}_2\text{NH}_2$ unit and approximately one millimole of lithium aluminum hydride, which had been purified by an ether extraction, was added to a reaction tube. The tube was evacuated and approximately ten milliliters of ether was distilled and condensed in the tube at $-196^\circ\text{C}$. The reaction mixture was warmed to $0^\circ\text{C}$ and maintained at this temperature for approximately twelve hours. After cooling the tube to $-196^\circ\text{C}$, only 0.114 millimoles of hydrogen was measured in the Toepler system.

**TABLE 20**

**INFRARED SPECTRUM OF AMINOBORANE FROM ETHER REACTION**

<table>
<thead>
<tr>
<th>Frequency (cm.$^{-1}$)</th>
<th>Intensity</th>
<th>Frequency (cm.$^{-1}$)</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>3320-3220</td>
<td>s</td>
<td>1220-1150</td>
<td>s, br</td>
</tr>
<tr>
<td>2380-2280</td>
<td>s, br</td>
<td>1050</td>
<td>sh</td>
</tr>
<tr>
<td>1575</td>
<td>m</td>
<td>880</td>
<td>sh</td>
</tr>
<tr>
<td>1405</td>
<td>m</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Intensities: s = strong; m = medium; w = weak; sp = sharp; br = broad; sh = shoulder.

Experiments were undertaken to produce hydrogen by the attack of a protonic substance on the hydridic hydrogen of aminoborane. Under the inert nitrogen atmosphere of a dry box, aminoborane and ammonium chloride were added to a reaction tube. The tube was evacuated and dry ammonia was
distilled and condensed in the tube at -196°C. The ammonia solution was kept at -78°C. for twenty hours and the solution was then frozen to -196°C. No hydrogen was generated. Also, no hydrogen was generated at room temperature when gaseous hydrogen chloride or a hydrogen chloride ether solution was mixed with aminoborane.

Since methanol protolysizes aminoborane, the degree of hydrolysis of aminoborane with water was investigated. Under the inert nitrogen atmosphere of a dry box, 35.1 milligrams of aminoborane was added to a reaction tube. The tube was evacuated and five milliliters of water distilled and condensed above the aminoborane at -196°C. The system was warmed to room temperature. After two hours, the system was cooled to -196°C. and 0.780 millimoles of hydrogen were measured by the Toepler system. This was 28 per cent of the available hydridic hydrogen.

Unlike water and methanol, tert-butyl alcohol does not react vigorously with aminoborane. A reaction tube containing 32.2 milligrams of aminoborane was evacuated and five milliliters of tert-butyl alcohol was condensed above the aminoborane at -196°C. Since tert-butyl alcohol has a melting point of 25°C., the system was warmed above 25°C. After three hours the mixture was cooled to -196°C. and the hydrogen evolved measured in the Toepler system. Only 0.191 millimoles of hydrogen was produced, which was 8.6 per cent of the available hydridic hydrogen.
8. **Analysis**

Analysis of aminoborane from the ether reaction by acid hydrolysis at 100°C. gave erratic and low results. A good analysis was obtained by acid hydrolysis only when the hydrolysis tube was heated at 165°C. for ten days and by the Rittner and Culmo method when the sample was digested in H$_2$SO$_4$ for several days at 360°C. The results using these two methods are given in Table 21.

**TABLE 21**

ANALYSIS OF AMINOBORANE

<table>
<thead>
<tr>
<th>%Boron</th>
<th>%Nitrogen</th>
<th>%Hydridic Hydrogen</th>
<th>B:N:H</th>
</tr>
</thead>
<tbody>
<tr>
<td>90.8</td>
<td>89.4</td>
<td>91.23</td>
<td>1.02:1.00:2.04</td>
</tr>
</tbody>
</table>

*Percentages are given as experimental value/theoretical value based on 100 per cent pure aminoborane.*

The other approximately ten per cent is diethyl ether, carbon analyses gave 6.11 and 5.41 per cent. Also a total hydrogen analysis, whose theoretical value is 13.97 per cent, gave values on different samples of 14.34 and 12.69 per cent.

When the aminoborane was heated under vacuum at 60°C. for several days, the carbon and hydrogen per cent decreased—3.54 per cent carbon and 10.89 per cent hydrogen; 3.65 per cent carbon and 8.93 per cent hydrogen.
G. Miscellaneous Reactions

1. Reaction of lithium methylnamide with diborane in diethyl ether

Bissot and Parry (25) have reported the preparation of crystalline N, N', N"-trimethylcyclotriborazane, \((\text{MeEBE}_2)^3\), which sublimes in vacuo at 100°C. Therefore the reaction of lithium methylnamide with diborane in diethyl ether was undertaken in order to determine if \((\text{MeHNEH}_2)_3\) would be formed. An amorphous material plus lithium borohydride was obtained.

Under the inert nitrogen atmosphere of a dry box, 9.13 millimoles of LiMeNH was added to a 100 milliliter bulb which was fitted with a 24/40 joint. Previously recorded was the total weight of the 100 milliliter bulb, teflon encased stirring bar which was to be used to stir the reaction, and a rubber serum cap which was to be used to cap the bulb. By means of a stopcock adaptor, the bulb was evacuated and approximately forty-five milliliters of diethyl ether was distilled and condensed into the bulb at -78°C. After the mixture was frozen to -196°C, 12.35 millimoles of diborane was condensed above the mixture. The system was immersed in a beaker containing a Dry Ice-isopropyl alcohol. While the mixture was stirred by a magnetic stirring bar, the reaction was followed at -78°C. by observing the disappearance of lithium methylnamide which is insoluble in diethyl ether. Within ten minutes a
partially clear solution was present. The solution was warmed to \(-10^\circ\text{C}\). and then the clear solution was frozen to \(-196^\circ\text{C}\). Only a trace amount of hydrogen had been evolved. Unreacted diborane was distilled from the reaction at \(-78^\circ\text{C}\), passed through a trap at \(-140^\circ\text{C}\), and recovered in a trap at \(-196^\circ\text{C}\). The recovered diborane was 2.91 millimoles, which is 0.31 millimoles less than the theoretical value for a one to one mole reaction. Ether was removed by distillation and the remaining white, solid product was dried in the vacuum system for one day.

Under the inert nitrogen atmosphere of a dry box, the bulb was capped with the rubber serum cap and weighed. The products weighed 534 milligrams as opposed to a theoretical weight of 582 milligrams. An X-ray powder pattern of the products gave only "d" values for lithium borohydride. None of the product sublimed in vacuo on heating to 180°C.

2. **The reaction of lithium amide with diborane in tetrahydrofuran and in dimethyl ether**

The reaction of lithium amide with diborane in solvents other than diethyl ether was undertaken. A typical experiment involved the reaction of nine millimoles of lithium amide with an excess of diborane to yield lithium borohydride and amorphous aminoborane. Under the inert nitrogen atmosphere of a dry box, a weighed quantity of
lithium amide was added to a 100 milliliter bulb which was fitted with a 24/40 joint. The bulb was evacuated and forty-five milliliters of tetrahydrofuran was distilled and condensed into the bulb. After freezing the mixture to -196°C., diborane was condensed above the mixture. The system was then immersed in a Dry Ice-isopropyl alcohol bath of -78°C. and was stirred. Reaction was followed at -78°C. by observing the disappearance of lithium amide which was insoluble in tetrahydrofuran. After two hours a clear solution was formed. Tetrahydrofuran and unreacted diborane were removed by distillation. Complete removal of tetrahydrofuran could be carried out only at room temperature and in some cases a paste remained. Under the inert nitrogen atmosphere of a dry box, the white, solid products were recovered. An X-ray powder diffraction pattern of the solid products gave only "d" values for lithium borohydride.

The reaction of lithium amide with diborane in dimethyl ether was carried out in a similar manner and the same results were obtained. On removal of the last traces of dimethyl ether at room temperature from the products, small traces of hydrogen were evolved.

3. The reaction of sodium amide with diborane in diethyl ether.

The reaction of sodium amide with diborane in diethyl ether produced negligible reaction at room temperature over
a period of weeks. A typical experiment involved 3.08 millimoles of sodium amide and 4.22 millimoles of diborane in ether to give only a trace amount of sodium borohydride and amorphous aminoborane. Under the inert nitrogen atmosphere of the dry box, the sodium borohydride was added to a reaction bulb which was fitted with a 24/40 $\mathsf{E}$ joint. By means of a stopcock adaptor, the bulb was evacuated and approximately forty milliliters was distilled and condensed into the bulb at $-78^\circ\text{C}$. After the mixture was frozen to $-196^\circ\text{C}$, the diborane was condensed above the solid mixture. The system was then left at room temperature for two and one-half weeks and stirred periodically. Diethyl ether and unreacted diborane were then removed by distillation.

Under the inert nitrogen atmosphere of a dry box, the remaining white solid was recovered. An X-ray powder diffraction pattern of the solid gave "d" values for sodium amide and sodium borohydride as given in Table 22. Only the lines with "d" values of 3.56, 3.09, 1.86, and 1.78 belong to sodium borohydride; the remaining lines are from unreacted sodium amide.
TABLE 22
X-RAY POWDER DIFFRACTION PATTERN
OF THE REACTION OF SODIUM AMIDE WITH DIBORANE
IN ETHER

<table>
<thead>
<tr>
<th>Intensity</th>
<th>d(Å)</th>
<th>Intensity</th>
<th>d(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>vs</td>
<td>5.2</td>
<td>s</td>
<td>2.18</td>
</tr>
<tr>
<td>vw</td>
<td>3.56</td>
<td>m</td>
<td>2.07</td>
</tr>
<tr>
<td>m</td>
<td>3.40</td>
<td>m</td>
<td>2.02</td>
</tr>
<tr>
<td>s</td>
<td>3.20</td>
<td>s</td>
<td>1.97</td>
</tr>
<tr>
<td>m</td>
<td>3.09</td>
<td>vw</td>
<td>1.86</td>
</tr>
<tr>
<td>s</td>
<td>3.01</td>
<td>w</td>
<td>1.84</td>
</tr>
<tr>
<td>m</td>
<td>2.71</td>
<td>vw</td>
<td>1.78</td>
</tr>
<tr>
<td>w</td>
<td>2.50</td>
<td>w</td>
<td>1.734</td>
</tr>
<tr>
<td>vw</td>
<td>2.36</td>
<td>w</td>
<td>1.627</td>
</tr>
<tr>
<td>s</td>
<td>2.24</td>
<td>w</td>
<td>1.567</td>
</tr>
<tr>
<td></td>
<td></td>
<td>w</td>
<td>1.501</td>
</tr>
</tbody>
</table>

Intensities: v = very; w = weak; m = medium; s = strong.
III. DISCUSSION OF RESULTS

A. Reactions of Bases with Diammoniate of Diborane in Liquid Ammonia

1. Reaction of sodium acetylide with diammoniate of diborane

Sodium acetylide reacts rapidly with diammoniate of diborane in liquid ammonia to produce sodium borohydride, acetylene, ammonia, and cycloborazanes.

\[ \text{NaC}^-\text{CH} + \text{BH}_2(\text{NH}_3)_2\text{BH}_4 \rightarrow \text{NaBH}_4 + \text{HC}^-\text{CH} \]

The strongly basic anion, \( \text{C}^-\text{CH}^- \), abstracts a protonic hydrogen from the quaternary nitrogen of \( \text{BH}_2(\text{NH}_3)_2^+ \) to form acetylene and \( \text{H}_2\text{NBH}_2\text{NH}_2 \). Polymerization occurs by the following association process.

\[ \text{H}_2\text{N}^-\text{B}^-\text{NH}_2 \]

\[ \text{H}_2\text{N}^-\text{BH}_2\text{NH}_2 \rightarrow \text{H}_3\text{NBH}_2\text{NH}_2\text{BH}_2\text{NH}_2 + \text{NH}_3 \]

to give

\[ 5\text{H}_3\text{NBH}_2\text{NH}_2 \rightarrow \text{H}_3\text{N}(\text{BH}_2\text{NH}_2)_5 + \text{NH}_3 \]

Cyclization then occurs through elimination of ammonia to produce cyclopentaborazane, which precipitates.

\[ \text{H}_3\text{N}(\text{BH}_2\text{NH}_2)_5 \rightarrow (\text{BH}_2\text{NH}_2)_5 + \text{NH}_3 \]
from the ammonia solution. Low yields of the ammonia soluble cyclotriborazane are obtained also from this reaction.

2. **Reaction of sodium amide with diammoniate of diborane**

Sodium amide reacts with diammoniate of diborane in liquid ammonia to produce sodium borohydride, ammonia, and cyclopentaborazane (large scale reactions gave one percent yields of cyclotriborazane and cyclodiborazane (56).

\[
\text{NaNH}_2 + \text{BH}_2(\text{NH}_2)_2\text{BH}_4 \rightarrow \text{NaBH}_4 + 2\text{NH}_3 + \frac{1}{5}(\text{BH}_2\text{NH}_2)_5
\]

The mechanism for the formation of cyclopentaborazane is the same as that of the reaction of sodium acetylide with diammoniate of diborane, in which the basic anion abstracts a proton from the ammonia coordinated to the \( \text{BH}_2(\text{NH}_2)_2^+ \) cation. Preliminary studies in this laboratory indicate that the association process is very rapid. Polymerization produces chains greater than 2 or 3 \( \text{BH}_2\text{NH}_2 \) units within half an hour (62), which is the usual time for all the sodium amide to react with diammoniate of diborane. This is in accord with the observation that if the ammonia solvent is removed before or after precipitation occurs, cyclopentaborazane is still found to be the predominant species.
3. Reaction of metallic sodium with diammoniate of diborane

Cyclopentaborazane is also the predominant species formed in the reaction of metallic sodium and diammoniate of diborane in liquid ammonia. The sodium reduces the protonic hydrogen of the ammonia on the cation, $BH_2(NH_3)_2^+$,

$$Na + BH_2(NH_3)_2^+ \rightarrow Na^+ + H_3NBH_2NH_2 + 1/2H_2$$

to give an overall reaction of

$$Na + BH_2(NH_3)_2BH_4 \xrightarrow{NH_3} NaBH_4 + NH_3 + 1/2H_2 + (BH_2NH_2)_5$$

Presumably association of the $BH_2NH_2$ species occurs in the same manner as described in the previous cases.

a. Cycloborazanes

The cycloborazanes, isolated from the reactions of sodium acetylide, sodium amide, and metallic sodium with diammoniate of diborane in liquid ammonia, are crystalline, white solids which are stable in moist air and in methanol. Cyclotriborazane, which sublimes at 100°C. in vacuo, is soluble in ammonia and many organic solvents. On the other hand, cyclopentaborazane is not soluble in ammonia and most organic solvents. Dimethyl sulfoxide and dimethyl formamide are the only known solvents for cyclopentaborazane. Cyclopentaborazane shows more resistance towards protonic attack than cyclotriborazane.

It is of interest to note that Dahl and Schaeffer synthesized cyclotriborazane (49) by starting with the
six-membered borazine ring; they assumed that it remained intact throughout the steps required to produce cyclotriborazane. On the other hand, reactions in this investigation with diammoniate of diborane produced $\text{BH}_2\text{NH}_2$ units which underwent self-association.

B. Reaction of Lithium Amide with Diborane in Diethyl Ether

Lithium amide reacts with diborane in diethyl ether to produce aminoborane, which has an average chain length of four $\text{BH}_2\text{NH}_2$ units, and lithium borohydride.

$$\text{LiNH}_2 + \text{B}_2\text{H}_6 \overset{\text{Et}_2\text{O}}{\rightarrow} \text{LiBH}_4 + 1/4(\text{BH}_2\text{NH}_2)_{\text{Av.},4}$$

The aminoborane is a white, amorphous solid which does not sublime. It is not stable in moist air or in methanol. Heating aminoborane to 60°C in order to remove the diethyl ether absorbed on it causes decomposition. Dimethyl sulfoxide and ammonia are the only known solvents for aminoborane.

Two possible reaction schemes, which have been suggested by Schaeffer and Basile (42), involve the addition of a $\text{BH}_3$ unit to the amide, followed by displacement of the aminoborane by the stronger acid, $\text{BH}_3$.

$$\text{LiNH}_2 + \text{BH}_3 \rightarrow \text{LiBH}_3\text{NH}_2$$

$$\text{LiBH}_3\text{NH}_2 + \text{BH}_3 \rightarrow \text{LiBH}_4 + \text{H}_2\text{BNH}_2$$
and the addition of $2\text{BH}_3$ units to the amide ion

$$2\text{BH}_3 + \text{LiNH}_2 \rightarrow \text{LiH}_2\text{N(BH}_3\text{)}_2$$

to form a salt which then cleaves to form lithium borohydride and aminoborane.

Perhaps a more likely scheme involves the unsymmetrical cleavage of diborane by the amide ion.

$$\text{LiNH}_2 + \text{BH}_2\text{H} \rightarrow \text{LiBH}_4 + \text{BH}_2\text{NH}_2$$

The aminoborane formed from the reaction of lithium amide with diborane probably forms a weak addition compound with solvent, $\text{Et}_2\text{O}$.

$$\text{BH}_2\text{NH}_2 + \text{Et}_2\text{O} \rightarrow \text{Et}_2\text{O.BH}_2\text{NH}_2$$

Polymerization occurs probably by the following association process

$$\text{Et}_2\text{OBH}_2\text{NH}_2 \rightarrow \text{Et}_2\text{O(BH}_2\text{NH}_2\text{)}_2 + \text{Et}_2\text{O}$$

to give

$$4\text{Et}_2\text{OBH}_2\text{NH}_2 \rightarrow \text{Et}_2\text{O(BH}_2\text{NH}_2\text{)}_{4\text{v}} + 3\text{Et}_2\text{O}$$

The polymeric aminoborane then precipitates from solution with an $\text{Et}_2\text{O}$ molecule weakly coordinated to the terminal $\text{BH}_2$ group. Further polymerization is prevented by the
insolubility of the aminoborane. The majority of the weakly coordinated ether molecules are removed from the aminoborane by vacuum distillation at room temperature. Analyses of the aminoborane showed that only about ten per cent by weight of the product was absorbed ether, which gives a $\text{BH}_2\text{NH}_2$ to $\text{Et}_2\text{O}$ ratio or 23.1 to 1.00.

The molecular weight of aminoborane, determined cryoscopically in ammonia and dimethylsulfoxide, varies from three to five $\text{BH}_2\text{NH}_2$ units from sample to sample obtained from the $\text{LiNH}_2-\text{B}_2\text{H}_6$ reaction in diethyl ether. The aminoborane most likely is a heterogenous mixture with an average molecular species of $4\text{BH}_2\text{NH}_2$ units. The reason for the heterogenous mixture and samples of varying molecular weight is probably due to the relatively low solubility of the aminoborane and the difficulty involved in duplicating the exact experimental procedures from run to run.

Protolysis studies undertaken in methanol and water show discontinuities in the protolysis curves in Figure 9 which indicate that two types of hydrogen are protolized; one type is rapidly protolized, while the second type is protolized much more slowly. The easily attacked hydridic hydrogen probably comes from a terminal $\text{BH}_2$ group, indicating a chain-like structure. In contrast, the cycloborazanes in which all of the borons are quaternary are stable in methanol and water. The rapidly attacked hydridic hydrogen accounts for approximately 30 per cent of the available
hydridic hydrogen per \( \text{BH}_2\text{NH}_2 \), which indicates a chain length of about 3 1/2 \( \text{BH}_2\text{NH}_2 \) units. It must be noted that Table 15 and 16 and Figure 9 are based on 100 per cent purity of aminoborane, whereas, if the aminoborane were merely a mixture of \( \text{(BH}_2\text{NH}_2)_4 \) and ten per cent by weight of ether there would be an apparent 22.5 per cent of rapidly protolized hydrogen as opposed to 25.0 per cent. From infrared spectra, lithium borohydride was shown to be present occasionally in very small quantities. A one per cent contamination of lithium borohydride in a sample of 99 per cent pure \( \text{(BH}_2\text{NH}_2)_4 \) would cause the rapidly protolized hydrogen to appear to be 27.7 per cent. Thus these two factors tend to cancel each other.

Therefore the molecular weights and the protolysis studies of the aminoborane from the lithium amide-diborane reaction in diethyl ether are consistent and indicate that the predominant species are open chains of low molecular weights with an average of \( 4\text{BH}_2\text{NH}_2 \).

Attempts to form cyclic polymers from the acyclic aminoborane of the \( \text{LiNH}_2\text{-B}_2\text{H}_6 \) reaction have failed. No satisfactory explanation can be given as to why the aminoborane does not form a cyclic compound, especially in liquid ammonia. Because ammonia is a stronger base than ether, one would expect that in ammonia \( 3\text{N(BH}_2\text{NH}_2)_4 \) species would be formed and would cyclize in a manner identical to that described in the ammonia reactions. One possible explanation
is that the acyclic aminoborane is stabilized through the formation of hydrogen bridges as in the case of aminodiborane.

For example, in the case of $(\text{BH}_2\text{NH}_2)_4$, the boron on the terminal BH$_2$ group (first boron atom in the polymer) could form a hydrogen bridge bond with the hydridric hydrogen on the third or fourth boron atom in the chain.

This satisfies the tendency for boron to be quaternary, but spectroscopic evidence for a hydrogen bridged bond in aminoborane was not found. Molecular models made of the above examples in which hydrogen bridging occurs show that such models are sterically favorable and would be readily attacked by protonic substances, but that the attack by an ammonia molecule would be sterically restrained from forming an addition compound with the aminoborane.

C. Summary

It is apparent from the results presented in this dissertation that the BH$_2$NH$_2$ species obtained from reactions
in liquid ammonia are neither amorphous nor highly polymeric substances, as reported in the earlier literature (12,40,41,42). The aminoborane obtained in the ether reaction is amorphous as reported by Schaeffer and Basile (42), but is not highly polymeric. The main difference between the reactions in ammonia and ether is that the BH₂NH₂ species are cyclic and non-cyclic, respectively. Species obtained from ammonia systems can be recrystallized from water and from methanol without apparent protolysis. On the other hand, the BH₂NH₂ material obtained from the ether reaction is easily protolized by these solvents. Furthermore, the species isolated from the ammonia reactions can be obtained free of solvent; while in the ether reaction the BH₂NH₂ species are never isolated free of ether at room temperature. Heating to 60°C. partially removes some of the absorbed ether, however, this produces decomposition, indicated by the generation of hydrogen. The reactions in ammonia form cycloborazane species that are stable to 120°C. under vacuum.
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AUTOBIOGRAPHY

I, Cecil William Hickam, Jr., was born in Pulaski, Virginia, August 3, 1939. I attended secondary school there and graduated from Pulaski High School in June 1956. I attended Washington and Lee University, Lexington, Virginia, where I received the Bachelor of Science degree in Chemistry and a commission in the Army Chemical Corps in June 1960. In the autumn of 1960 I enrolled at The Ohio State University in the Department of Chemistry. While in residence there, I held a Du Pont Fellowship for the summers of 1963 and 1964, and a General Electric Fellowship for the school year of 1963-1964. During the school years of 1960-1961 and 1962-1963 I was a teaching assistant in chemistry. My research for the Doctor of Philosophy Degree has been under the supervision of Dr. Sheldon G. Shore.