This dissertation has been microfilmed exactly as received 67-10,935

YOUNG, David Edward, 1940-
ISOLATION AND REACTIONS OF ORGANOBORANE HETEROCYCLES CONTAINING HYDROGEN BRIDGES.

The Ohio State University, Ph.D., 1967
Chemistry, inorganic

University Microfilms, Inc., Ann Arbor, Michigan
ISOLATION AND REACTIONS OF ORGANOBORANE HETEROCYCLES
CONTAINING HYDROGEN BRIDGES

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

By

David Edward Young, B.S., M.Sc.

* * * * *

The Ohio State University
1967

Approved by

Adviser
Department of Chemistry
ACKNOWLEDGMENTS

This work was supported financially by a grant from the National Science Foundation for which I am grateful.

I am indebted to Professor Sheldon G. Shore for his continued encouragement and guidance throughout my graduate studies. I appreciate the stimulating discussions with him which led to a more enthusiastic approach to the problem on my part. The fact that the solution to this problem was attained is indicative of Dr. Shore’s knowledge of chemical principles and problems.

I am grateful to my colleagues, Dr. Don T. Dix and Mr. Russell A. Geanangel, who willingly discussed the problem and often offered valuable advice.

I am most grateful for the support of my wife, Susan. Her unfailing patience and moral support have been invaluable.
VITA

February 6, 1940 Born—Beaumont, Texas

1962 . . . . . B.S., Baylor University, Waco, Texas

1962-1963 . . . University Fellow, Department of Chemistry, The Ohio State University, Columbus, Ohio

1963-1964 Teaching Assistant, Department of Chemistry, The Ohio State University, Columbus, Ohio

1964-1967 . . . Research Assistant, Department of Chemistry, The Ohio State University, Columbus, Ohio

1965 . . . . . M.Sc., The Ohio State University, Columbus, Ohio

PUBLICATIONS


FIELD OF STUDY

Major Field: Inorganic Chemistry

Studies Dealing with the Chemistry of Boron. Professor Sheldon G. Shore
CONTENTS

ACKNOWLEDGMENTS ........................................ 11
VITA ........................................................ iii
TABLES ................................................... vi
ILLUSTRATIONS .......................................... vii

I. INTRODUCTION ...................................... 1
   A. Historical Background ........................ 1
      1. Organoboranes from hydroboration of dienes 2
      2. Cleavage of the borane hydrogen bridge system 4
   B. Statement of Problem ........................ 7

II. EXPERIMENTAL ...................................... 11
   A. Apparatus ...................................... 11
   B. Starting Materials .......................... 16
   C. Analytical Procedures ........................ 23
   D. 1,2-Tetramethylenediborane ................. 23
      1. Preparation ............................... 23
      2. Properties ............................. 25
      3. Boron-11 nuclear magnetic resonance spectrum 25
      4. Infrared spectrum ........................ 27
   E. 1,2-Bis(tetramethylene)-diborane ........... 29
      1. Preparation ............................... 29
<table>
<thead>
<tr>
<th>CONTENTS—continued</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2. Properties</td>
<td>33</td>
</tr>
<tr>
<td>3. Mass spectrum</td>
<td>33</td>
</tr>
<tr>
<td>4. Boron-11 nuclear magnetic resonance spectrum</td>
<td>36</td>
</tr>
<tr>
<td>5. Proton nuclear magnetic resonance</td>
<td>37</td>
</tr>
<tr>
<td>6. Infrared spectrum</td>
<td>38</td>
</tr>
<tr>
<td>F. Hydrogen Bridge Cleavage Reactions</td>
<td>40</td>
</tr>
<tr>
<td>1. 1,2-Tetramethylenediborane</td>
<td>40</td>
</tr>
<tr>
<td>2. 1,2-Bis(tetramethylene)-diborane</td>
<td>43</td>
</tr>
<tr>
<td>3. Molecular weight of the trimethylamine, dimethylamine and methylamine adducts of 1,2-bis(tetramethylene)-diborane</td>
<td>48</td>
</tr>
<tr>
<td>4. Boron-11 nuclear magnetic resonance spectra of cleavage products</td>
<td>52</td>
</tr>
<tr>
<td>III. DISCUSSION OF RESULTS</td>
<td>61</td>
</tr>
<tr>
<td>BIBLIOGRAPHY</td>
<td>81</td>
</tr>
</tbody>
</table>
### TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Infrared Spectrum of 1,2-Tetramethylene-diborane</td>
<td>27</td>
</tr>
<tr>
<td>2. Mass Spectrum of 1,2-Bis(tetramethylene)-diborane</td>
<td>35</td>
</tr>
<tr>
<td>3. Boron-11 Nuclear Magnetic Resonance Data for Diboranes</td>
<td>37</td>
</tr>
<tr>
<td>4. Infrared Spectrum of 1,2-Bis(tetramethylene)-diborane</td>
<td>40</td>
</tr>
<tr>
<td>5. Description of the Boron-11 Nuclear Magnetic Resonance Spectra of Cleavage Products</td>
<td>54</td>
</tr>
<tr>
<td>6. Boron-11 Nuclear Magnetic Resonance Data</td>
<td>55</td>
</tr>
<tr>
<td>7. Molecular Weight Data from Dioxane Solutions</td>
<td>69</td>
</tr>
<tr>
<td>8. Boron-11 Nuclear Magnetic Resonance Data</td>
<td>72</td>
</tr>
<tr>
<td>9. Boron-11 Nuclear Magnetic Resonance Data</td>
<td>75</td>
</tr>
<tr>
<td>10. Relative Yields of Symmetrical and Unsymmetrical Cleavage Products</td>
<td>77</td>
</tr>
</tbody>
</table>
## ILLUSTRATIONS

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Infrared Gas Cell</td>
<td>14</td>
</tr>
<tr>
<td>2.</td>
<td>Five mm. Nuclear Magnetic Resonance Sample Tubes</td>
<td>17</td>
</tr>
<tr>
<td>3.</td>
<td>Fifteen mm. Nuclear Magnetic Resonance Sample Tubes</td>
<td>18</td>
</tr>
<tr>
<td>4.</td>
<td>Storage Bulb</td>
<td>20</td>
</tr>
<tr>
<td>5.</td>
<td>Boron-11 Nuclear Magnetic Resonance Spectrum of 1,2-Tetramethylenediborane</td>
<td>26</td>
</tr>
<tr>
<td>6.</td>
<td>Infrared Spectrum of 1,2-Tetramethylene-diborane</td>
<td>28</td>
</tr>
<tr>
<td>7.</td>
<td>Reaction Apparatus with U-Tube Trap</td>
<td>31</td>
</tr>
<tr>
<td>8.</td>
<td>Mass Spectrum of 1,2-Bis(tetramethylene)-diborane</td>
<td>34</td>
</tr>
<tr>
<td>9.</td>
<td>Infrared Spectrum of 1,2-Bis(tetramethylene)-diborane</td>
<td>39</td>
</tr>
<tr>
<td>10.</td>
<td>Boron-11 Nuclear Magnetic Resonance Spectra of N(CH₃)₃ and NH₂CH₃ Reaction Products of 1,2-Tetramethylenediborane</td>
<td>57</td>
</tr>
<tr>
<td>11.</td>
<td>Boron-11 Nuclear Magnetic Resonance Spectra of NH₂CH₃ Reaction Product of 1,2-Tetramethylenediborane at Selected Temperatures</td>
<td>58</td>
</tr>
<tr>
<td>12.</td>
<td>Boron-11 Nuclear Magnetic Resonance Spectra of NH₂CH₃ and NH₃ Reaction Products of 1,2-Bis(tetramethylene)-diborane</td>
<td>59</td>
</tr>
<tr>
<td>13.</td>
<td>Infrared Spectra of &quot;Bis-boracyclopentane&quot; and 1,2-Bis(tetramethylene)-diborane</td>
<td>65</td>
</tr>
<tr>
<td>14.</td>
<td>Infrared Spectra of &quot;Boracyclopentane-borane&quot; and 1,2-Tetramethylenediborane</td>
<td>68</td>
</tr>
</tbody>
</table>
I. INTRODUCTION

A. Historical Background

In recent years there has been intensive study of organoborane compounds. In general, the organoboranes can be discussed in two types of formulations: those having B-C bonds and those having B-A-C bonds where A is taken to represent an atom such as oxygen, nitrogen, or sulfur.

In both types of compounds, it is generally conceded that the cyclic species is more stable than its acyclic counterpart (1) and thus, in many cases, more amenable to study. Maitlis has published an extensive review of heterocyclic organic boron compounds in general (2), and doctoral dissertations by S. H. Rose (3) and B. Z. Egan (4) contain thorough literature references on B-O-R and B-S-R compounds. In this discussion, "organoborane" will be taken to mean compounds where the boron atom is bound to carbon.

Ring compounds based on boron and carbon atoms have been known only a few years (5). The availability of new syntheses for this type of organoboron compound and the fact that the handling of materials sensitive to air and moisture no longer presents a problem in preparation and characterization has led to rapid development in this area.
For many years the only practical route to organoboranes involved the reaction of organometallic compounds with the boron ester or halide (6,7). The first boron-carbon ring compounds were also prepared in this manner in the reaction of phenylboron difluoride and dilithium alkanes (5). The resulting products were phenylboracyclopentane and phenylboracyclohexane.

\[
\text{C}_6\text{H}_5\text{BF}_2 + \text{Li} \xrightarrow{(\text{CH}_2)_n} \text{C}_6\text{H}_5\text{B}(\text{CH}_2)_n + 2\text{LiF}
\]

The observation that olefins could be readily converted into organoboranes under mild conditions provided a major new route to these compounds (8,9). A comprehensive discussion of the hydroboration of olefinic compounds can be found in Brown's "Hydroboration" (10).

1. Organoboranes from hydroboration of dienes

Köster reports that aliphatic boron heterocycles can be obtained simply and smoothly by hydroboration from dienes, the resulting products being colorless liquids distillable at reduced pressure without decomposition in some cases (11, 12,13).

\[
\text{B}_2\text{H}_6 + 3\text{C}_n\text{H}_{2n-2} \xrightarrow{\text{B}_2(\text{C}_n\text{H}_{2n})_3} \text{n=4,5,6}
\]
Köster also reports the isolation of bis-boracyclopentane from the hydroboration of 1,3-butadiene (14).

\[
\text{B}_{2}\text{H}_6 + 2 \rightarrow \text{bis-boracyclopentane}
\]

Bis-boracyclopentane exhibits many unusual properties such as no reaction with methanol below 100°, no reaction with olefins below 70°, and a bridge stretching frequency at 1612 cm\(^{-1}\) in the infrared spectrum. In contrast, Brown and Klender report that tetraorganodiboranes containing bulky alkyl groups react rapidly with terminal olefins and with methanol at 0° and exhibit the normal bridge absorption near 1555 cm\(^{-1}\) (15).

Brown reports that butadiene and diborane react at room temperature to form a polymeric organoborane with a molecular weight of 320 to 365 (10). The reaction mixture formed by the reaction of 2 moles of butadiene and 1 mole of diborane exhibits terminal B-H and bridge hydrogen stretching frequencies at 2500 and 1560 cm\(^{-1}\), respectively. The polymer reacts rapidly with methanol at room temperature. These results appear to be in conflict with those of Köster obtained from similar reaction conditions (14). It now appears that bis-borocyclopentane was obtained originally by Köster by the distillation of the initial reaction products at relatively high temperatures and must be a redistribution product of the material formed in the initial hydroboration stage (10), thereby
indicating that the initial reaction is not simple cyclization. Brown suggests that Köster's "bis-boracyclopentane" has properties which are more consistent with an isomeric structure containing a transannular boron hydrogen bridge system, 1,2-bis(tetramethylene)-diborane (I).

\[ \text{(I)} \quad \text{(II)} \]

1,2-Tetramethylenediborane (II) has been isolated from the elevated temperature gas phase hydroboration of butadiene in which diborane is in excess (16,17). The compound has been well characterized by its mass spectrum (16), its infrared spectrum (16), and its boron-11 and proton nuclear magnetic resonance spectra (16,17). The yield of 1,2-tetramethylenediborane in both cases is reported to be less than 35 per cent. The later study also included the reaction of diborane and allene which yielded 1,2-trimethylenediborane (17).

2. Cleavage of the borane hydrogen bridge system

The simplest example of cleavage of a borane hydrogen bridge system resulting in Lewis acid-base adduct formation
is the reaction of diborane with trimethylamine (18).

\[
\begin{array}{c}
\text{H} \quad \text{H} \quad \text{B} \quad \text{H} \\
\text{H} \quad \text{H} \quad \text{B} \quad \text{H} \\
\end{array}
\quad + \quad 2 \text{N(CH}_3\text{)}_3 \quad \rightarrow \quad 2 \text{(CH}_3\text{)}_3\text{NBH}_3
\]

This type of cleavage in which the diborane molecule forms products containing BH\textsubscript{3} groups is commonly called "symmetrical cleavage." The cleavage reaction involves the rupture of the electron deficient bridge bonds, which have a significant energy of formation. Modern values for dimerization of borane, 2BH\textsubscript{3} = B\textsubscript{2}H\textsubscript{6}, have been reported to be approximately -36 to -38 kcal/mole (19, 20, 21). Typical Lewis bases which cleave the diborane molecule symmetrically are CO (22), tetrahydrofuran (23), (CH\textsubscript{3})\textsubscript{2}PH (24), (CH\textsubscript{3})\textsubscript{3}P (25), and (CH\textsubscript{3})\textsubscript{2}S (26).

Diborane, however, is capable of reacting with other electron pair donors to produce ionic products, BH\textsubscript{2}L\textsubscript{2} BH\textsubscript{4}\textsuperscript{−}, where L represents the donor species. In cases such as these, the reaction is called an "unsymmetrical cleavage" reaction, implying the following scheme:

\[
\begin{array}{c}
\text{H} \quad \text{B} \quad \text{H} \\
\text{H} \quad \text{H} \quad \text{B} \quad \text{H} \\
\end{array}
\quad + \quad 2\text{L} \quad \rightarrow \quad \text{BH}_2\text{L}_2 \quad \text{BH}_4\textsuperscript{−}
\]

The controlled addition of diborane to ammonia leads to apparent unsymmetrical cleavage of the hydrogen-bridged bonds, resulting in the formation of the "diammoniate of diborane" [bis(diammine)dihydroboron(l\textsuperscript{+})hydroborate] (22, 25, 27, 28, 29, 30, 31, 32, 33). Direct reaction of diborane with an
amine containing an N-H bond has been shown in the cases of 
NH₂CH₃ and NH(CH₃)₂ to lead to a mixture of symmetrical and 
unsymmetrical cleavage products (34). Earlier literature 
suggested that simple borane adducts are formed in these 
reactions (35,36,37).

Although many factors are probably involved in deter­
mining the course of cleavage, one major factor is most 
likely steric, considering the change in type of cleavage 
observed with progressive methyl substitution on nitrogen in 
the methyl amines. Relative yields of cleavage products from 
individual reactions of diborane with CH₃NH₂, (CH₃)₂NH, and 
(CH₃)₃N were found to be the following (34):

\[
\begin{align*}
H₂B(NH₂CH₃)₂ & \quad BH₄^- \quad \gg \quad H₂BNH₂CH₃ \\
H₃BNH(CH₃)₂ & \quad H₂B[NH(CH₃)₂]₂ \quad BH₄^- \\
H₃BN(CH₃)₃ & \quad \text{only detectable product}
\end{align*}
\]

In addition to the amine bases cited above, 
dimethylsulfoxide is the only other well-documented example 
of a base which produces unsymmetrical cleavage upon reaction 
with diborane (38).

Boron-11 nuclear magnetic resonance spectroscopy has 
proved to be the most successful method for distinguishing 
symmetrical and unsymmetrical cleavage products of the re­
actions of Lewis bases and diborane (34,38). The number of 
protons which are directly bonded to boron determines the
multiplet structure of the boron-11 nmr spectrum, provided other atoms which are bonded to boron have nuclei which do not spin couple with the boron nucleus.

Evidence has been found which indicates that cleavage of the bridge system of diborane takes place in stepwise fashion with the first step involving the rupture of one bridge bond,

\[ \text{H}_2\text{B}-\text{H}-\text{BH}_3 \]

while the second step involves the rupture of the second bridge bond, with the point of attack determining whether the cleavage is symmetrical or unsymmetrical (30,32). The postulated intermediates in the reaction of diborane with trimethylamine and ammonia have been prepared and studied by boron-11 nmr (39,40).

B. Statement of Problem

The examples of stable organodiboranes are few (10,14, 16,17). It was discussed earlier that there is controversy concerning the existence of \textit{bis}-boracyclopentane, which seems to be the most stable organodiborane with respect to thermal decomposition, reaction with olefins, and hydrolysis or alcoholysis (13). Köster has provided some details of the derivative chemistry of this compound which suggest that it is \textit{bis}-boracyclopentane (41). On the other hand, Brown has
suggested that "bis-boracyclopentane" has properties which are more consistent with the isomeric 1,2-bis(tetramethylene)-diborane (I) (10).

1,2-Tetramethylenediborane (II) has been prepared by two different research groups (16,17). The infrared and boron-11 nmr spectra of this compound lend credence to the structure of the product, which contains but one terminal B-H bond for each boron. Köster studied the equilibration of the presumed bis-boracyclopentane and diborane at 100° (13, 41). The product of this reaction was assigned the structure (III) on the basis of its infrared spectrum.

![Structure III](image)

The published spectrum, however, militates against this structure in that a sharp singlet at 2510 cm⁻¹ is observed, providing evidence for but one terminal B-H bond for each boron atom. If >BH₂ were present, as Köster states, a doublet representing symmetric and asymmetric terminal B-H stretching frequencies would be observed in the region 2600 to 2500 cm⁻¹ (10,43,44). Indeed, the infrared spectrum of (III) appears to be identical to that of 1,2-tetramethylenediborane (II).
Because of the controversy involving the structure of the hydroboration product of 2 moles of butadiene and 1 mole of diborane, further study of this system and the system involving equimolar amounts of the two reactants was carried out. Included in this study were procedures comparable to those of Köster (14). The problem was approached primarily from a synthetic point of view, in that the main objectives were the preparation, isolation, and characterization of reaction products. The development of a convenient, high-yield synthetic route to 1,2-tetramethylenediborane was one result of this study. Because infrared and boron-11 nmr spectroscopy do not easily distinguish between bis-boracyclopentane,

![bis-boracyclopentane](image)

and 1,2-bis(tetramethylene)-diborane,

![1,2-bis(tetramethylene)-diborane](image)

cryoscopic molecular weight determinations were carried out on Lewis base cleavage derivatives to determine the actual structure of the compound. It should be noted that cleavage of the bridge system should yield two particles in the case of bis-boracyclopentane and one particle in the case of 1,2-bis(tetramethylene)-diborane. A natural extension of such an investigation was the study of the products obtained from the diboranes by reaction with the methyl-substituted amines.
and ammonia. Boron-11 nmr spectroscopy was used to determine whether symmetrical or unsymmetrical cleavage resulted in each case. The multiplicity of the spectra clearly differentiated between the two types of products.
II. EXPERIMENTAL

A. Apparatus

1. Vacuum system

Because of the extreme sensitivity of diborane to air and moisture and the hydrolytic instability of the reaction products, all reactants and products were manipulated in a standard vacuum system similar to that described by Sanderson (45). The vacuum apparatus consisted of a pumping section, a main manifold, four reaction trains, two of which could be separated into two independent sections by means of vacuum stopcocks, a calibrated distillation train, three storage bulbs, and a calibrated Töpler system. Volumes were calibrated with carbon dioxide or sulfur hexafluoride by standard procedures and checked with carbon dioxide samples from other calibrated systems.

The pumping system consisted of a high capacity Duo-Seal forepump and a three stage mercury diffusion pump filled with triple distilled mercury, which could be bypassed when necessary to avoid oxidation or contamination of the hot mercury. Cold traps cooled with liquid nitrogen preceded both the forepump and the mercury diffusion pump.

The reaction trains contained several reaction stations consisting of a standard taper 14/35 inner joint separated
from the reaction manifold by a 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 through an auxiliary manifold. On these reaction trains, materials were introduced into the vacuum system and reactions were carried out.

The distillation train consisted of five individually calibrated traps of total volume in excess of one-half liter and four mercury manometers. The traps could be used as a unit or individually. The train was used for low temperature fractionation of gaseous mixtures as well as for measurement of condensible gases.

Each three-liter storage bulb was connected to a mercury manometer and a U-tube trap. Two of the bulbs were equipped with mercury float valves to prevent contact of gases with any stopcock lubricant. As an added precaution against leakage, a stopcock was placed between the mercury float valve and the vacuum system.

An auxiliary vacuum system made of 1/4 inch copper tubing was used to operate the mercury float valves and the Töpler pump.

2. Handling of reactants

Reactions were generally carried out in glass vessels with standard taper joints which could be separated from the
mercury "blowouts" by a vacuum stopcock adapter. Some reactions were carried out under greaseless conditions through the use of Fischer and Porter Company Teflon vacuum stopcocks. Non-volatile materials were introduced into the reaction vessel in the dry nitrogen atmosphere of a dry-box and were subsequently transferred to the vacuum system without exposure to air or moisture.

3. Infrared spectra

Infrared spectra were run in the gas phase using a cell with windows of Eastman Kodak's infrared transmitting material, "IRTRAN-4" as shown in Figure 1. The cell was equipped with a vacuum stopcock so that it could be charged on the vacuum line. Solution spectra were obtained in Perkin Elmer matched solution cells with NaCl plates. The instrument used to obtain spectra in the 2.5 to 16 micron region was the Perkin-Elmer 337 recording grating spectrometer. Each spectrum was calibrated by superimposing the spectrum of polystyrene on it.

4. Nuclear magnetic resonance spectra

Boron-11 nuclear magnetic resonance spectra were obtained using a Varian HR-60 high resolution spectrometer, and proton spectra were obtained with a Varian A-60 spectrometer equipped with integrator. Low temperature nuclear magnetic resonance spectra were obtained by using a Varian variable temperature probe assembly in which pre-cooled
Figure 1. Infrared gas cell.
nitrogen gas was passed over the sample tube. Spectra obtained with the HR-60 spectrometer were calibrated by use of sidebands of known frequency separation from a standard signal due to an external reference of trimethylborate or boron trifluoride etherate.

5. Mass spectra

Mass spectra were obtained using an Associated Electrical Instruments, Ltd., Model MS10 mass spectrometer.

6. Töpler system

Gaseous reaction products were first passed through a U-tube trap at liquid nitrogen temperature before entering the Töpler pump. The trap was filled with 1/4 inch glass helices for greater cold surface. The Töpler pump was an Eck and Krebs type 4100. The gasometer system, equipped with an auxiliary demountable bulb to give greater volume, had been calibrated with carbon dioxide following standard procedures.

7. Glassware

All glassware, prior to use, was washed in alcoholic potassium hydroxide, rinsed with distilled water, rinsed with dilute hydrochloric acid, rinsed again with distilled water, rinsed with acetone, left in an oven at 125°C for several hours, and then taken to the vacuum line or to the dry-box while still above room temperature.
8. Reaction vessels incorporating nuclear magnetic resonance sample tubes

Four different types of apparatus were used to prepare 5 and 15 mm. nmr sample tubes. In the case of the 5 mm. sample tubes, the volatile reactants and solvent were either distilled directly into the sample tube fitted with a Fischer and Porter Company Teflon vacuum stopcock where they were allowed to react at the desired temperature, or they were distilled into vessels equipped with nmr tube sidearms into which the reaction mixture could be poured following reaction in the vessel. The two types of apparatus are shown in Figure 2.

In the case of the 15 mm. sample tubes, the volatile reactants were either distilled directly into the sample tube and allowed to react as above, or the sample tube was charged in the dry-box, fitted with a vacuum adapter, attached to the vacuum and pumped on after the contents were frozen, and then sealed with a torch. These two types of apparatus are shown in Figure 3.

B. Starting Materials

1. Diborane

Diborane was obtained from Gallery Chemical Company. It was purified by low temperature fractional distillation and stored at liquid nitrogen temperature in the vacuum system. Measurement was made as a gas at room temperature.
Figure 2. Five mm. nuclear magnetic resonance sample tubes.
Figure 3. Fifteen mm. nuclear magnetic resonance sample tubes.
2. **1,3-Butadiene**

Instrument grade 1,3-butadiene was obtained from the Matheson Company. It was purified by low temperature fractional distillation and stored at -80°C in the vacuum system. Measurement was made as a gas at room temperature.

3. **Trimethylphosphine**

Trimethylphosphine was prepared from the reaction of methyl magnesium bromide and phosphorus trichloride in ether. The trimethylphosphine was stabilized as the solid tetrameric monomiodotrimethylphosphine silver complex \([(\text{CH}_3)_3\text{P} \rightarrow \text{AgI}]_4\), by reaction of silver iodide in aqueous potassium iodide solution (46,47). The trimethylphosphine could be freed from the complex at elevated temperature.

4. **Trimethylamine**

Reagent grade trimethylamine was dried at 0°C with calcium hydride on the vacuum line. The dry material was stored at room temperature in a vessel such as shown in Figure 4. The material was measured as a gas at room temperature, after which it was distilled into the reaction vessel in the vacuum system.

5. **Dimethylamine**

Anhydrous dimethylamine was obtained from the Matheson Company. It was taken from the cylinder into the vacuum system where it was measured as a gas at room temperature.
Figure 4. Storage bulb.

Fischer-Porter
4mm quick open
in line valve
Cat. No.
795-120-0004
6. **Methylamine**

Anhydrous methylamine was obtained from the Matheson Company. It was dried over sodium and was stored at -80°C. It was measured as a gas at room temperature in the vacuum system.

7. **Ammonia**

Anhydrous ammonia was obtained from the Matheson Company. In some cases it was fractionated on the vacuum system before measurement, and in others it was taken straight from the cylinder and used with no treatment.

8. **Tetrahydrofuran**

Reagent grade tetrahydrofuran was dried with lithium aluminum hydride on the vacuum system. It was stored at room temperature in a vessel as shown in Figure 4. The dry material was distilled into the reaction vessel in the vacuum system.

9. **Diethyl ether**

Reagent grade absolute ether was dried with lithium aluminum hydride on the vacuum system and stored at room temperature in the manner described above. The dry material was distilled into the reaction vessel in the vacuum system.

10. **Diisopropyl ether**

Practical grade diisopropyl ether was dried with lithium aluminum hydride and then with calcium hydride in
the vacuum system. The dry material was stored at room
temperature as above and was distilled into the reaction
vessel in the vacuum system.

11. Di-n-butyl ether

Practical grade di-n-butyl ether was dried with lithium
aluminum hydride and then with calcium hydride in the vacuum
system. The dry material was distilled into the reaction
vessel in the vacuum system.

12. Dichloromethane

Spectroquality dichloromethane was dried with calcium
hydride in the vacuum system. It was stored at room tempera­
ture in the grease-free vessels described, and the dry
material was distilled into the reaction vessel in the
vacuum system.

13. 1,4-Dioxane

Reagent grade 1,4-dioxane was dried with lithium
aluminum hydride and then with calcium hydride in the vacuum
system. It was stored at room temperature in the previously
described manner, and the dry material was distilled into the
reaction vessel in the vacuum system.

14. Acetonitrile

Spectroquality acetonitrile was dried with calcium
hydride in the vacuum system. It was stored at room
temperature as above, and the dry material was distilled into the reaction vessel in the vacuum system.

C. Analytical Procedures

In cases where applicable, infrared spectroscopy was used to determine the purity of reaction products. Molecular weights were determined by mass spectrometry and by cryoscopy measurements in dioxane. Nitrogen was determined by the Kjeldahl method, and hydridic hydrogen was liberated by acid hydrolysis and measured in the Töpler system.

Reaction stoichiometries were determined by measuring the amounts of starting materials and the amounts of excess materials recovered.

D. 1,2-Tetramethylenediborane

1. Preparation

The molecule 1,2-tetramethylenediborane was synthesized from diborane and 1,3-butadiene in various ether solvents. The reaction gave approximately the same yield in diethyl ether, diisopropyl ether, and di-n-butyl ether; however, because it was more easily separated in the pure form from di-n-butyl ether, most of the reactions were carried out in this solvent.

Approximately 25 ml. of the dry solvent was distilled into an evacuated 250 ml. reaction bulb equipped with a Teflon covered magnetic stirring bar and connected to the vacuum line with a Fischer and Porter Teflon stopcock adapter.
A measured amount of 1,3-butadiene was then condensed in the bulb which was cooled with liquid nitrogen. The bulb was allowed to warm to room temperature, and the contents were stirred to obtain a homogeneous solution. The solution was then frozen with liquid nitrogen, and a measured amount of diborane in slight excess to the amount of 1,3-butadiene was condensed in the bulb. With the stopcock closed, the bulb and adapter were then removed from the vacuum line, and stirring was started as soon as the solvent had melted sufficiently. The reaction mixture was allowed to stir at room temperature for about an hour, and then a heating bath was placed under the bulb and stirring was continued at 45° to 50° for periods of time ranging from three to ten days. The reaction bulb was then allowed to cool to room temperature. The bulb was placed on the vacuum line where fractionation of the volatile materials in the reaction mixture was accomplished to yield pure 1,2-tetramethylenediborane. Repeated fractionation through a Skelly Solve F slush bath (-140°) to liquid nitrogen on the distillation train removed the unreacted traces of diborane. Then repeated fractionation through a chlorobenzene slush bath (-45°) removed the crude product from di-n-butyl ether which remained in the -45° trap. From the crude material, which contained some isomeric 1,2-(1'-methyltrimethylene)-diborane, pure 1,2-tetramethylenediborane could then be isolated by repeated fractionation through a trap at Dry Ice temperature. The
desired material remained in the Dry Ice trap. In addition to the volatile materials of the reaction, some viscous, non-volatile liquid was formed which remained in the reaction bulb. Heating of this material, which is probably polymeric organoborane product, to approximately 100° yielded additional amounts of 1,2-tetramethylenediborane.

In a typical experiment, 10 mmoles of 1,3-butadiene was allowed to react with 12 mmoles of diborane. From this reaction about 6 to 7 mmoles of pure 1,2-tetramethylenediborane was isolated.

2. Properties

1,2-Tetramethylenediborane is a clear, colorless liquid at room temperature. It has a vapor pressure of 26.3±0.1 mm. at 0° (16). It is soluble in most organic solvents, and decomposes only slightly at room temperature over a period of two to three days, with the formation of diborane (16).

3. Boron-11 nuclear magnetic resonance spectrum

The boron-11 nuclear magnetic resonance spectrum of 1,2-tetramethylenediborane is shown in Figure 5. The spectrum consists basically of a doublet, each member of which is a partially resolved triplet. The $J_{BH}$ value of 129±2 cps and the $J_{BHB}$ value of 40±2 cps as well as the chemical shift value of -22.6 ppm with respect to $BF_3\cdot Et_2O$
Figure 5. Boron-11 nuclear magnetic resonance spectrum of 1,2-tetramethylene-diborane.
agree with the latest literature values reported for the compound (17).

The sample tube was prepared by distilling the compound directly into a 5 mm. nmr sample tube attached to the vacuum line. Then tetrahydrofuran was added as solvent, and while the contents were frozen at liquid nitrogen temperature the tube was sealed with a torch. The contents were then allowed to mix before the spectrum was obtained.

4. **Infrared spectrum**

A typical spectrum of 1,2-tetramethylenediborane in the vapor phase at room temperature is shown in Figure 6. The absorption bands given in Table 1 represent both the data obtained in this investigation and the literatures values. The compound was allowed to expand into an infrared cell with "IRTRAN 4" windows, such as shown in Figure 1, to about 20 mm. pressure, and the spectrum was obtained.

<table>
<thead>
<tr>
<th>Frequency (cm.⁻¹)</th>
<th>Intensity^a</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>Literature</td>
<td></td>
</tr>
<tr>
<td>2910</td>
<td>2930</td>
<td>s</td>
</tr>
<tr>
<td>2890</td>
<td></td>
<td>sh</td>
</tr>
<tr>
<td>2840</td>
<td></td>
<td>w</td>
</tr>
<tr>
<td>2510</td>
<td>2510</td>
<td>s</td>
</tr>
<tr>
<td>1575</td>
<td>1580</td>
<td>vs</td>
</tr>
<tr>
<td>1465</td>
<td>1460</td>
<td>w</td>
</tr>
<tr>
<td>1410</td>
<td>1420</td>
<td>m</td>
</tr>
<tr>
<td>1310</td>
<td>1300</td>
<td>mw</td>
</tr>
<tr>
<td>1120</td>
<td>1120</td>
<td>s</td>
</tr>
<tr>
<td>875</td>
<td>870</td>
<td>m</td>
</tr>
</tbody>
</table>

^aIntensities: s=strong; m=medium; w=weak; sh=shoulder; v=very.
Figure 6. Infrared spectrum of 1,2-tetramethylenediborane.
E. 1,2-Bis(tetramethylene)-diborane

1. Preparation

1,2-Bis(tetramethylene)-diborane was prepared from four reactions, each of which was performed under different conditions.

A 2:1 mole ratio of 1,3-butadiene and diborane was allowed to react in tetrahydrofuran at room temperature for several hours in the first reaction. Approximately 20 ml. of the dry solvent was distilled into an evacuated reaction tube equipped with a Teflon covered magnetic stirring bar and connected to the vacuum line with a Fischer and Porter Teflon stopcock adapter. A measured amount of diborane was then condensed in the tube which was cooled with liquid nitrogen. The tube was allowed to warm to room temperature, and the contents were stirred to obtain a homogeneous solution. The solution was then frozen in liquid nitrogen and the correct amount of 1,3-butadiene was condensed in the tube. With the stopcock closed, the tube and adapter were removed from the vacuum line, and stirring was started as soon as the solvent had melted sufficiently. As the solution warmed, care had to be taken to prevent too vigorous a reaction. At approximately 10° the reaction begins to froth and must be quenched by cooling the reaction with liquid nitrogen for a few seconds. After this period the reaction was allowed to continue to warm and proceeded smoothly to room temperature. The reaction tube was then reattached to the vacuum system and
all volatile materials were removed from the reaction mixture. A viscous, non-volatile organoborane polymer remained in the tube. At this point, dry nitrogen was let into the tube and a U-tube trap was attached to the reaction tube by means of a jointed take-off as shown in Figure 7. The apparatus was attached to the vacuum system by means of the stopcock adapter on the U-tube, and evacuated. The polymeric material was then heated to above 125°, and the volatile rearrangement products were continuously pumped through the trap cooled with a -80° bath. No additional volatile product was collected in the trap after approximately one hour of heating. Dry nitrogen was again let into the apparatus, and the original reaction tube was replaced with a collection tube. The product was found to distill slowly at room temperature and was collected in the collection tube cooled to -80° at which temperature the liquid product was frozen. Subsequent distillation to a storage tube completed the purification of the material, which was identified as 1,2-bis(tetramethylene)-diborane.

A typical reaction involved 12 mmoles of diborane and 24 mmoles of 1,3-butadiene from which could be obtained approximately 10 mmoles of pure product.

In a second reaction 2 mmoles of 1,2-tetramethylene-diborane was allowed to react with 2 mmoles of 1,3-butadiene for two days in tetrahydrofuran at 40°. Both reactants were measured in the vacuum line and distilled into a reaction
Figure 7. Reaction apparatus with U-tube trap.
tube, equipped with a magnetic stirring bar and a Teflon adapter along with the solvent. The reaction mixture was allowed to warm with stirring to room temperature and was then placed in a 40° bath. At the end of the reaction period, the solvent was removed from the reaction at 0°, leaving the reaction product behind. This product was then distilled at 40° from the reaction tube. No polymeric product was produced in the reaction. The distilled product was identical to that of the first reaction.

A third reaction was carried out between butadiene and diborane in tetrahydrofuran following the procedure described for the first reaction. In this case the mole ratio of butadiene to diborane was 1:1 instead of 2:1. Again, as in the case of the 2:1 reaction discussed first, a polymeric material was formed. The solvent removed from the polymeric material was treated with trimethylamine on the vacuum line, and the solids that resulted after the removal of the excess amine and the tetrahydrofuran were identified as the trimethylamine adducts of diborane and 1,2-tetramethylenediborane. The polymeric material was heated to above 120°, and the volatile rearrangement products were collected in the U-tube trap which was cooled to liquid nitrogen temperature. Fractionation of the rearrangement products revealed both 1,2-tetramethylenediborane, which was identified by its B11 nmr spectrum, and 1,2-bis(tetramethylenê)-diborane as products of the 1:1 reaction.
In a fourth reaction it was shown that \textit{1,2-bis (tetramethylene)-diborane} could be prepared in diisopropyl ether solvent by using the same procedure discussed earlier for the preparation of \textit{1,2-tetramethylenediborane}. Instead of using a slight excess of diborane, a 2:1 mole ratio of butadiene to diborane was employed. After removal of the solvent at 0°, the less volatile reaction product was distilled at 40° into a sidearm attached to the reaction tube. Some non-volatile polymeric material was also formed in the reaction.

2. Properties

\textit{1,2-Bis(tetramethylene)-diborane} is a clear, colorless liquid at room temperature and has a vapor pressure of approximately 1 mm. at 25°. It shows no tendency to decompose at room temperature upon standing. \textit{1,2-Bis(tetramethylene)-diborane} melts at approximately -30°.

3. Mass spectrum of \textit{1,2-bis(tetramethylene)-diborane}

A standard representation of the mass spectrum of \textit{1,2-bis(tetramethylene)-diborane} is given in Figure 8, and the corresponding data are given in Table 2. The spectrum of the vapor at 100° shows a parent mass at a m/e ratio of 136, the calculated molecular weight of the compound.

The mass spectra of the products obtained from the first three preparative methods discussed were identical in every respect. The mass spectra of the first and last fractions
Figure 8. Mass spectrum of $1,2$-bis(tetramethylene)-diborane.
<table>
<thead>
<tr>
<th>m/e</th>
<th>Ratio (%)</th>
<th>m/e</th>
<th>Ratio (%)</th>
<th>m/e</th>
<th>Ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>8</td>
<td>54</td>
<td>22</td>
<td>95</td>
<td>16</td>
</tr>
<tr>
<td>13</td>
<td>14</td>
<td>55</td>
<td>12</td>
<td>96</td>
<td>4</td>
</tr>
<tr>
<td>14</td>
<td>10</td>
<td>56</td>
<td>16</td>
<td>97</td>
<td>0</td>
</tr>
<tr>
<td>15</td>
<td>24</td>
<td>57</td>
<td>1</td>
<td>98</td>
<td>0</td>
</tr>
<tr>
<td>16</td>
<td>14</td>
<td>58</td>
<td>2</td>
<td>99</td>
<td>0</td>
</tr>
<tr>
<td>17</td>
<td>0</td>
<td>59</td>
<td>0</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>18</td>
<td>0</td>
<td>60</td>
<td>1</td>
<td>101</td>
<td>0</td>
</tr>
<tr>
<td>19</td>
<td>0</td>
<td>61</td>
<td>0</td>
<td>102</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>0</td>
<td>62</td>
<td>2</td>
<td>103</td>
<td>0</td>
</tr>
<tr>
<td>21</td>
<td>0</td>
<td>63</td>
<td>14</td>
<td>104</td>
<td>2</td>
</tr>
<tr>
<td>22</td>
<td>0</td>
<td>64</td>
<td>27</td>
<td>105</td>
<td>4</td>
</tr>
<tr>
<td>23</td>
<td>0</td>
<td>65</td>
<td>14</td>
<td>106</td>
<td>8</td>
</tr>
<tr>
<td>24</td>
<td>4</td>
<td>66</td>
<td>18</td>
<td>107</td>
<td>6</td>
</tr>
<tr>
<td>25</td>
<td>10</td>
<td>67</td>
<td>16</td>
<td>108</td>
<td>0</td>
</tr>
<tr>
<td>26</td>
<td>58</td>
<td>68</td>
<td>2</td>
<td>109</td>
<td>0</td>
</tr>
<tr>
<td>27</td>
<td>82</td>
<td>69</td>
<td>0</td>
<td>110</td>
<td>0</td>
</tr>
<tr>
<td>28</td>
<td>100</td>
<td>70</td>
<td>0</td>
<td>111</td>
<td>0</td>
</tr>
<tr>
<td>29</td>
<td>24</td>
<td>71</td>
<td>0</td>
<td>112</td>
<td>0</td>
</tr>
<tr>
<td>30</td>
<td>2</td>
<td>72</td>
<td>0</td>
<td>113</td>
<td>0</td>
</tr>
<tr>
<td>31</td>
<td>1</td>
<td>73</td>
<td>0</td>
<td>114</td>
<td>0</td>
</tr>
<tr>
<td>32</td>
<td>4</td>
<td>74</td>
<td>0</td>
<td>115</td>
<td>0</td>
</tr>
<tr>
<td>33</td>
<td>2</td>
<td>75</td>
<td>1</td>
<td>116</td>
<td>0</td>
</tr>
<tr>
<td>34</td>
<td>8</td>
<td>76</td>
<td>2</td>
<td>117</td>
<td>0</td>
</tr>
<tr>
<td>35</td>
<td>0</td>
<td>77</td>
<td>8</td>
<td>118</td>
<td>0</td>
</tr>
<tr>
<td>36</td>
<td>0</td>
<td>78</td>
<td>20</td>
<td>119</td>
<td>0</td>
</tr>
<tr>
<td>37</td>
<td>12</td>
<td>79</td>
<td>18</td>
<td>120</td>
<td>0</td>
</tr>
<tr>
<td>38</td>
<td>16</td>
<td>80</td>
<td>10</td>
<td>121</td>
<td>0</td>
</tr>
<tr>
<td>39</td>
<td>60</td>
<td>81</td>
<td>4</td>
<td>122</td>
<td>1</td>
</tr>
<tr>
<td>40</td>
<td>40</td>
<td>82</td>
<td>2</td>
<td>123</td>
<td>2</td>
</tr>
<tr>
<td>41</td>
<td>88</td>
<td>83</td>
<td>0</td>
<td>124</td>
<td>4</td>
</tr>
<tr>
<td>42</td>
<td>16</td>
<td>84</td>
<td>0</td>
<td>125</td>
<td>3</td>
</tr>
<tr>
<td>43</td>
<td>26</td>
<td>85</td>
<td>0</td>
<td>126</td>
<td>0</td>
</tr>
<tr>
<td>44</td>
<td>4</td>
<td>86</td>
<td>0</td>
<td>127</td>
<td>0</td>
</tr>
<tr>
<td>45</td>
<td>10</td>
<td>87</td>
<td>0</td>
<td>128</td>
<td>0</td>
</tr>
<tr>
<td>46</td>
<td>0</td>
<td>88</td>
<td>0</td>
<td>129</td>
<td>0</td>
</tr>
<tr>
<td>47</td>
<td>0</td>
<td>89</td>
<td>0</td>
<td>130</td>
<td>0</td>
</tr>
<tr>
<td>48</td>
<td>1</td>
<td>90</td>
<td>0</td>
<td>131</td>
<td>0</td>
</tr>
<tr>
<td>49</td>
<td>2</td>
<td>91</td>
<td>1</td>
<td>132</td>
<td>0</td>
</tr>
<tr>
<td>50</td>
<td>10</td>
<td>92</td>
<td>2</td>
<td>133</td>
<td>0</td>
</tr>
<tr>
<td>51</td>
<td>14</td>
<td>93</td>
<td>6</td>
<td>134</td>
<td>4</td>
</tr>
<tr>
<td>52</td>
<td>16</td>
<td>94</td>
<td>14</td>
<td>135</td>
<td>8</td>
</tr>
<tr>
<td>53</td>
<td>44</td>
<td>136</td>
<td>14</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
of any particular reaction yield were also found to be identical in every respect.

4. Boron-11 nuclear magnetic resonance spectrum of 1,2-bis(tetramethylene)-diborane

Typical boron-11 nuclear magnetic resonance spectra of 1,2-bis(tetramethylene)-diborane were obtained for the products from all of the preparative methods discussed. A sealed capillary containing boron trifluoride etherate was inserted into each nmr tube as an external reference. All spectra consisted of a broadened single peak with no resolution of boron-bridge hydrogen spin coupling even at 100°. The chemical shift of the peak was found to be -28.5 ppm in each case which is consistent with the expected shift to lower magnetic field strength with alkyl substitution.

The sample tubes were prepared by distilling the compound directly into a 5 mm. nmr tube attached to the vacuum line. Either tetrahydrofuran or dioxane was then distilled into the tubes as solvent, and while the contents were frozen, the tubes were sealed with a torch.

A comparison of boron-11 nmr data for diborane and the organodiboranes is shown in Table 3.
### TABLE 3
BORON-11 NUCLEAR MAGNETIC RESONANCE DATA FOR DIBORANES

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\delta^a\text{(ppm)})</th>
<th>(J_{BH_t}\text{(cps)})</th>
<th>(J_{BH_b}\text{(cps)})</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diborane(^b)</td>
<td>-17.6</td>
<td>137</td>
<td>48</td>
<td></td>
</tr>
<tr>
<td>1,2-Tetramethylene-diborane</td>
<td>-22.6</td>
<td>129</td>
<td>40</td>
<td>THF</td>
</tr>
<tr>
<td>1,2-Bis(tetramethylene)-diborane</td>
<td>-28.5</td>
<td>--</td>
<td>c</td>
<td>THF</td>
</tr>
</tbody>
</table>

\(^a\)BF\(_3\)OEt\(_2\) reference.


\(^c\)Unresolved in boron-11 spectrum.

5. Proton-nuclear magnetic resonance spectrum of 1,2-bis(tetramethylene)-diborane

The proton nmr spectrum of 1,2-bis(tetramethylene)-diborane was obtained from a dichloromethane solution. The spectrum showed only two signals in addition to the reference solvent signal. The higher field resonance is assigned to the four CH\(_2\) groups attached to boron (\(\tau = 9.22\)), and the other resonance is assigned to the remaining four CH\(_2\) groups (\(\tau = 8.45\)). These values agree favorably with those obtained from another investigation involving 1,2-tetramethylenediborane (17). Splitting due to H-H spin interactions is not observed; however, the resonance signals are rather broad.
The expected multiplet structure due to the bridge hydrogens was not observed. This is probably due to the fact that the more intense peaks in the septet structure are most likely masked by the observed higher field resonance, as expected from the work of Lindner and Onak (17).

6. Infrared spectrum of 1,2-bis(tetramethylene)-diborane

The infrared spectra of 1,2-bis(tetramethylene)-diborane were obtained in the vapor phase from the products of the first three preparative methods discussed. A small amount of the material was condensed in the sidearm of the infrared gas cell shown in Figure 1. The material was allowed to warm to room temperature where it has a vapor pressure of approximately 1 mm. At this low pressure, only the C-H stretching frequency at 2911 cm\(^{-1}\) and the bridge hydrogen stretching frequency at 1614 cm\(^{-1}\) were observed. Mild heating of the cell increased the intensity of these absorptions, and other weak absorptions were observed.

The complete infrared spectrum was obtained from a dichloromethane solution of the compound and is shown in Figure 9. The absorption bands given in Table 4 represent data which were obtained from this spectrum.
Figure 9. Infrared spectrum of 1,2-bis(tetramethylene)-diborane.
TABLE 4

INFRARED SPECTRUM OF 1,2-BIS(TETRAMETHYLENE)-DIBORANE

<table>
<thead>
<tr>
<th>Frequency (cm.(^{-1}))</th>
<th>Intensity(^a)</th>
<th>Frequency (cm.(^{-1}))</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>2905</td>
<td>s</td>
<td>1207</td>
<td>w</td>
</tr>
<tr>
<td>2842</td>
<td>ms</td>
<td>1160</td>
<td>s</td>
</tr>
<tr>
<td>2794</td>
<td>w</td>
<td>1075</td>
<td>w</td>
</tr>
<tr>
<td>2654</td>
<td>vw</td>
<td>1012</td>
<td>m</td>
</tr>
<tr>
<td>1808</td>
<td>w</td>
<td>969</td>
<td>w</td>
</tr>
<tr>
<td>1612</td>
<td>vs</td>
<td>939</td>
<td>m</td>
</tr>
<tr>
<td>1441</td>
<td>mw</td>
<td>871</td>
<td>w</td>
</tr>
<tr>
<td>1408</td>
<td>m</td>
<td>846</td>
<td>w</td>
</tr>
<tr>
<td>1333</td>
<td>w</td>
<td>817</td>
<td>m</td>
</tr>
<tr>
<td>1309</td>
<td>m</td>
<td>806</td>
<td>w</td>
</tr>
<tr>
<td>1215</td>
<td>w</td>
<td>780</td>
<td>mw</td>
</tr>
</tbody>
</table>

\(^a\)Intensities: s=strong; m=medium; w=weak; v=very.

F. Hydrogen Bridge Cleavage Reactions

1. 1,2-Tetramethylenediborane

1,2-Tetramethylenediborane was allowed to react with various Lewis bases to cleave the hydrogen bridge system and produce products of either symmetrical or unsymmetrical cleavage.

The trimethylamine adduct of 1,2-tetramethylenediborane was prepared by reacting \(N(CH_3)_3\) with the organodiborane in tetrahydrofuran with the amine in excess. The reactants were
distilled into a reaction vessel equipped with a vacuum stopcock adapter or into an nmr tube. The solvent was then condensed in the vessel, and the frozen contents were allowed to warm and mix. The reaction took place as the reactants mixed and resulted in the formation of the symmetrical cleavage product. In one reaction where the starting materials were carefully measured either by weighing or by use of the calibrated distillation train, measurement of the $N(CH_3)_3$ recovered set the reaction stoichiometry at a 2:1 amine to organodiborane mole ratio. The actual experimental value was found to be $1.98:1 = N(CH_3)_3$: organoborane. Typical reactions involved 1 mmole of the organodiborane and 3 to 4 mmoles of the amine. Analysis of a sample of the compound yielded the following results:

Found: \( \%N = 13.83; \%H \text{ (hydridic)} = 1.97 \)

Theory: \( \%N = 14.00; \%H \text{ (hydridic)} = 2.00 \)

The reaction of 1,2-tetramethylenediborane with dimethylamine was carried out in both liquid dimethylamine and dichloromethane as solvents in the same manner as that described for the $N(CH_3)_3$ reaction. The product of the reaction in both solvents proved to be the symmetrical cleavage product. In the case of the reaction in liquid dimethylamine, removal of the solvent after completion of the reaction left a solid product which, when dissolved in dichloromethane gave a boron-11 nmr spectrum identical to the product which was formed using dichloromethane as the solvent.
The reaction of 1,2-tetramethylenediborane with monomethyamine was carried out at -60° to -80° using methylamine as the solvent. The reactants were condensed in a reaction vessel described earlier, incorporating a 5 mm. nmr tube sidearm into which the reaction mixture was poured. The product was that of unsymmetrical cleavage of the bridge system, resulting in the inorganic Zwitter ion.

\[
\begin{align*}
\text{H}_2\text{BH} + 2 \text{NH}_2\text{CH}_3 & \xrightarrow{-80°} (\text{CH}_3\text{H}_2\text{N})^+ \text{BH}^{\text{-}} \text{BH}_3^-
\end{align*}
\]

The cleavage product decomposes at about -15° with the evolution of hydrogen, and extreme care was taken in preparing the nmr tube to insure that none of the material came into contact with glass surfaces warmer than the decomposition temperature. The entire reaction vessel with the nmr tube was immersed in a -80° bath before the solution was poured into the tube. The contents of the tube were then frozen in liquid nitrogen, and the tube was sealed with a torch. The reaction stoichiometry was set at 2:1 amine to organoborane mole ratio by measuring the NH$_2$CH$_3$ recovered from a reaction involving known amounts of starting material. The excess NH$_2$CH$_3$ was removed from the completed reaction at -40° and measured as a gas in the calibrated trap system.

The reaction of 1,2-tetramethylenediborane with ammonia was carried out in exactly the same manner as the
reaction with methylamine as described above. Again the reaction product was found to be the product of unsymmetrical cleavage, the inorganic Zwitter ion. The "diammoniate of 1,2-tetramethylenediborane" also decomposes at about -15° so that the same care had to be taken in preparing its nmr sample tube as in the methylamine case.

Trimethylphosphine was also reacted with 1,2-tetramethylenediborane in the manner described for the reaction with N(CH₃)₃. The product was identified as that involving symmetrical cleavage of the bridge system. The reaction solvent was tetrahydrofuran.

With the exception of the two unsymmetrical cleavage products, the compounds are stable and isolable as solids at room temperature in vacuo. Even in the case of the NH(CH₃)₂ adduct where hydrogen might be expected to be split out of the molecule, no such reaction was observed at 70° in dioxane. All of the products are vigorously hydrolyzed in acid solutions and slowly decompose in the air with the evolution of hydrogen.

2. 1,2-Bis(tetramethylene)-diborane

Reactions of 1,2-bis(tetramethylene)-diborane were carried out with various Lewis Bases. These bases reacted to produce products of either symmetrical or unsymmetrical cleavage of the hydrogen bridge system.
The trimethylamine adduct of 1,2-bis(tetramethylene)-diborane was prepared by reacting \(N(CH_3)_3\) with the organodiborane in either liquid \(N(CH_3)_3\) or in dioxane with the amine in excess. The reactants were distilled into a reaction vessel equipped with a Fischer and Porter Teflon stopcock, a Teflon covered magnetic stirring bar, and a 5 mm. nmr tube sidearm as shown in Figure 2. The solvent was then condensed in the vessel, and the frozen contents were allowed to warm and mix. As the reaction proceeded with stirring, a white solid formed which slowly dissolved in the solvent. The solution was then poured into the sidearm which was frozen in liquid nitrogen and sealed with a torch. The product of symmetrical cleavage was identified. Typical reactions involved approximately 0.5 mmole of the organodiborane with excess amine and 0.5 to 1 ml. of solvent.

The dimethylamine adduct of 1,2-bis(tetramethylene)-diborane was prepared using dimethylamine as both solvent and reactant. In the case of the dimethylamine adduct, solubility in the liquid base was appreciable. The reaction was carried out according to the exact procedure used for the \(N(CH_3)_3\) reaction, and the product of symmetrical cleavage resulted.

The reaction of 1,2-bis(tetramethylene)-diborane with monomethylamine was carried out in liquid methylamine at \(-60^\circ\). The solid adduct formed and did not go into solution until the reaction mixture was allowed to warm to
approximately -20°. The reaction was carried out in the same manner as the N(CH₃)₃ reaction except that temperatures were kept lower because the thermal stability of the expected unsymmetrical cleavage product was questionable. It was later found, however, that in the case of 1,2-bis(tetramethylene)-diborane, methylamine cleaves the bridge system symmetrically, and further studies were carried out with less regard for controlled temperature.

The stoichiometries of these reactions of 1,2-bis(tetramethylene)-diborane involving symmetrical cleavage will be discussed in the section concerning the molecular weights of the adducts.

The solid product of the reaction of 1,2-bis(tetramethylene)-diborane with NH₃ is not appreciably soluble in the liquid NH₃ solvent at temperatures below -30°. Again the apparatus used for the reaction was that described in Figure 2. Because of the limited solubility of the product in liquid ammonia, the reaction was allowed to proceed at -45° with vigorous stirring as a heterogeneous mixture for approximately 1 hr. After this time the NH₃ was slowly distilled from the reaction, and acetonitrile along with a small amount of NH₃ to insure excess ammonia was condensed in the reaction vessel cooled to -196°. Stirring of the mixture was begun as the reaction vessel warmed to -45°. At this temperature the product had limited solubility in the CH₃CN solvent, and a heterogeneous mixture resulted. The contents
were then allowed to warm slowly and because no evolution of hydrogen was observed due to decomposition of the product, ambient temperature was allowed. At this temperature the solid product slowly dissolved in the CH$_3$CN solvent. The product was identified as that involving unsymmetrical cleavage, and, in contrast to the unsymmetrical cleavage products of 1,2-tetramethylenediborane, it showed no tendency to decompose even upon standing at room temperature. The reaction was also carried out directly in CH$_3$CN with excess NH$_3$ with the same results.

In addition to the above products, the trimethylphosphine adduct of the organoborane was also prepared in the manner described for the reaction with N(CH$_3$)$_3$. The product was identified as the symmetrical cleavage product. The reaction was accomplished in tetrahydrofuran, dioxane, and glyme. The product showed no appreciable solubility in either trimethylphosphine or acetonitrile.

In contrast to the N(CH$_3$)$_3$ adduct of 1,2-tetramethylenediborane, the N(CH$_3$)$_3$ adduct of 1,2-bis(tetramethylene)-diborane appears to be slightly dissociated at room temperature as a solid and in solution. The percentage dissociation appears to be fairly small, but the fact that there is dissociation hindered efforts to obtain the adduct as a stoichiometrically pure solid and, thus, also hindered molecular weight determinations on the compound.
On the other hand, there is no apparent dissociation at room temperature of either the \((\text{CH}_3)_2\text{NH}\) or the \(\text{CH}_3\text{NH}_2\) adduct of 1,2-bis(tetramethylene)-diborane; however, both materials slowly evolve hydrogen at this temperature in contrast to the \((\text{CH}_3)_2\text{NH}\) adduct of 1,2-tetramethylenediborane. The evolution of hydrogen proceeds so slowly, however, that neither reaction stoichiometry nor molecular weight determinations are appreciably affected.

The reaction rates in the case of 1,2-bis(tetramethylene)-diborane with the Lewis bases appear to be much slower than those of the analogous reactions of 1,2-tetramethylenediborane. All of the products are vigorously hydrolyzed in acid solutions and slowly decompose in the air with the evolution of hydrogen.

It should be pointed out that in the cases where the liquid amines were used as solvents, closed systems capable of withstanding up to five atmospheres of pressure were employed safely. The apparatus was jointless and was equipped with a Fischer and Porter Teflon vacuum stopcock. The sealed nmr tubes were also capable of containing these pressures safely.

All of the reaction products were identified by their boron-11 nuclear magnetic resonance spectra. These spectra are discussed in a later section.
3. Molecular weight of the trimethylamine, dimethylamine, and methylamine adducts of 1,2-bis(tetramethylene)-diborane

As mentioned earlier, because of partial dissociation of the \( \text{N(CH}_3\text{)}_3 \) adduct of 1,2-bis(tetramethylene)-diborane in solution, molecular weight and reaction stoichiometry determinations were difficult to obtain with accuracy. The determination of the molecular weight was attempted cryoscopically in dioxane. A procedure for handling the material was employed which permitted a rough determination of the reaction stoichiometry and allowed the determination of the molecular weight to be made without actually handling the solid.

A portion of the organodiborane was condensed in a weighed vessel equipped with a Fischer and Porter Teflon stopcock, a magnetic stirring bar, and a jointed sidearm. The vessel was then reweighed to determine the amount of the organodiborane. A measured excess of \( \text{N(CH}_3\text{)}_3 \) was then condensed in the cold vessel along with dioxane, and the contents were allowed to warm. The reaction was stirred at room temperature for three days. The volatile materials of the solution were then fractionated until approximately one-half of the original solution remained in the tube. From the amount of \( \text{N(CH}_3\text{)}_3 \) recovered, an experimental value for the stoichiometry of the reaction of 1.94 \( \text{N(CH}_3\text{)}_3 \) to 1.00 \( \text{N(CH}_3\text{)}_3 \) organodiborane was obtained. The rest of the solvent was then removed from the vessel leaving a white solid which did not
appear to be completely free from liquid. To the solid about 12 ml. of dioxane was added, and the vessel was again weighed to determine the amount of dioxane. The freshly prepared solution was then covered with dry nitrogen and removed from the vacuum line. The solution was syringed into a closed molecular weight apparatus equipped with an electromagnetically controlled hopper stirrer and a Beckman thermometer. The apparatus had been flushed thoroughly with dry nitrogen. The solution concentration was 0.368 g. solute in 11.968 g. solvent, and the freezing point was depressed a maximum of 0.62°. This freshly prepared sample gave a molecular weight of 312; however, upon sitting for 18 hr., the sample showed a new molecular weight of 233. There was no change from this value upon further standing of the sample. The theoretical molecular weight for the adduct is 254.

Another sample of the adduct was prepared in a slightly different manner. A weighed amount of the organodiborane was treated with an excess of \( N(\text{CH}_3)_3 \), which acted as the solvent for the reaction, in a weighed vessel equipped with a Fischer and Porter Teflon right angle vacuum stopcock and a magnetic stirring bar. The solid adduct dissolved completely in the amine. The contents were stirred for three days, after which time the amine solvent was removed from the reaction vessel at room temperature. The amount of product was then determined by weighing the reaction vessel. Because of the partial dissociation of the adduct, the amount
of product in the reaction vessel was found to be less than expected because the dissociation products are volatile. Dioxane was then distilled in and measured as before. Transfer of the solution to the molecular weight apparatus followed by determination of the depression of the freezing point gave an initial molecular weight of 324 for the adduct. This value was found to slowly diminish over a period of 6 hr. until the value of 213 was reached. The solution concentration was 0.1052 g. solute in 10.783 g. solvent and the freezing point was depressed a maximum of 0.216°.

More meaningful reaction stoichiometry and molecular weight data were obtained from studies of the NH(CH₃)₂ and NH₂CH₃ adducts of 1,2-bis(tetramethylene)-diborane. As mentioned earlier, both adducts appear to be undissociated at room temperature although they do evolve hydrogen very slowly.

In the case of the NH(CH₃)₂ adduct, a weighed amount of the organodiborane was treated with an excess of NH(CH₃)₂ which acted as solvent for the reaction. The reaction vessel used was that described above, being capable of withstanding many atmospheres of pressure. The reaction was allowed to proceed for three days. During this period an amount of hydrogen was evolved which was approximately 5 per cent of the amount expected from total conversion of the adduct to the aminoborane. The excess amine was then removed from the reaction vessel, leaving a viscous, non-volatile liquid.
Although the adduct might possibly be a low melting solid when pure, the aminoborane impurity lowers this melting point so that the observation of the product as a liquid is not unreasonable. The amount of product was determined by weighing the reaction vessel. From two different experiments, reaction stoichiometries of 1.96 and 1.92 amine to 1.00 organoborane were obtained from the data. The solution concentrations were 0.2377 g. solute in 11.5475 g. solvent and 0.3208 g. solute in 9.5722 g. solvent, and the freezing point was depressed 0.436° and 0.694°, respectively. The molecular weights obtained from the dioxane solutions of the materials were 218 and 222. The theoretical molecular weight for the adduct is 226.

One of the solutions from which the molecular weights were obtained was then transferred to a 15 mm. nmr tube equipped with an external standard of trimethylborate. The boron-11 nmr spectrum showed the resonance doublet of the adduct which will be discussed later plus a very weak signal with a chemical shift in the region where monomeric aminoborane resonance signals generally occur. An infrared spectrum of a smear of the reaction product taken between NaCl plates clearly showed bands characteristic of NH and BH stretching at 3220 cm⁻¹ and 2300 cm⁻¹, respectively.

In the case of the NH₂CH₃ adduct, the exact same procedure was carried out to determine reaction stoichiometry and molecular weight that was employed in the case
of the NH(CH₃)₂ adduct. Again the reaction product was a viscous, non-volatile liquid. An experimental reaction stoichiometry value of 1.97 amine to 1.00 organoborane was obtained from the data gathered. The molecular weight was found to be 208. The solution concentration was 0.2890 g. solute in 10.0971 g. dioxane, and the freezing point depression was 0.614°. The theoretical molecular weight for the NH₂CH₃ adduct of 1,2-bis(tetramethylene)-diborane is 198.

Again the solution from which the molecular weight was obtained was transferred to a 15 mm. tube equipped with an external standard of trimethylborate, and the boron-11 spectrum was obtained. The only signal observed was the doublet due to the NH₂CH₃ adduct which is discussed in a later section.

4. Boron-11 nuclear magnetic resonance spectra of cleavage products

In all of the reactions of the organoboranes with the various Lewis bases, the type of cleavage product was identified by its boron-11 nuclear magnetic resonance spectrum. In all cases only one type of product was observed in the spectrum. As discussed earlier, of the ten products prepared, two were found to be thermally unstable, and the spectra of these products, uncomplicated by decomposition products, were obtained at temperatures ranging from -45° to -20°. These products were the unsymmetrical cleavage products from the reactions of 1,2-tetramethylenediborane
with \( \text{NH}_2\text{CH}_3 \) and \( \text{NH}_3 \). At these temperatures the signal for the positively charged boron was not observed. At higher temperatures superposition of the cation and decomposition product spectra makes analysis of the cation spectrum impossible. All other spectra were obtained at ambient temperature although it was found that better resolution of the spectra occurred at higher temperatures in some cases where the solvent was not a liquid amine.

The preparation of the sample tubes has been discussed previously. Each tube contained either a trimethylborate or a boron trifluoride etherate external standard which could be removed from the solution by inversion of the tube. Calibration of the spectra has also been discussed previously in this section.

Line broadening was found to occur with increasing alkyl substitution on the boron so that resolution decreases according to the following sequence:

\[
R_2BH^- < RBH_2^- < BH_3^-
\]

Table 5 shows the type of cleavage for each reaction and the multiplicity of the spectrum.

The multiplicity of the spectra is due to spin coupling of the \( \text{B-H} \) hydrogens \((J=1/2)\) with boron, and in the phosphine adducts is further complicated by the \( \text{P-B} \) spin coupling.
TABLE 5

DESCRIPTION OF THE BORON-11 NUCLEAR MAGNETIC RESONANCE SPECTRA OF CLEAVAGE PRODUCTS

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Type of Cleavage</th>
<th>Multiplicity of Spectrum</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-Tetramethylene-diborane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>+2N(CH₃)₃</td>
<td>Symmetrical</td>
<td>1:2:1 triplet</td>
</tr>
<tr>
<td>+2NH(CH₃)₂</td>
<td>Symmetrical</td>
<td>1:2:1 triplet</td>
</tr>
<tr>
<td>+2NH₂CH₂</td>
<td>Unsymmetrical</td>
<td>1:3:3:1 quartet</td>
</tr>
<tr>
<td>+2NH₃</td>
<td>Unsymmetrical</td>
<td>1:3:3:1 quartet</td>
</tr>
<tr>
<td>+2P(CH₃)₃</td>
<td>Symmetrical</td>
<td>1:2:1 triplet split into 3 1:1 doublets</td>
</tr>
</tbody>
</table>

| 1,2-Bis(tetramethylene)-diborane         |                  |                                        |
| +2N(CH₃)₃                                | Symmetrical      | 1:1 doublet                            |
| +2NH(CH₃)₂                               | Symmetrical      | 1:1 doublet                            |
| +2NH₂CH₂                                 | Symmetrical      | 1:1 doublet                            |
| +2NH₃                                    | Unsymmetrical    | 1:2:1 triplet for anion; singlet for cation |
| +2P(CH₃)₃                                | Symmetrical      | 1:1 doublet split into 2 1:1 doublets   |

The data gathered from the spectra are tabulated in Table 6. Included are data from similar B₂H₆ investigations.
<table>
<thead>
<tr>
<th>Compound</th>
<th>( \delta ) (ppm)</th>
<th>( J_{BH} ) (cps)</th>
<th>( J_{PB} ) (cps)</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>((CH_3)_3NBH_3^b)</td>
<td>+8.3</td>
<td>98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>((CH_3)_2NHBH_3^b)</td>
<td>+14.2</td>
<td>96</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH(_3)_NH(_2)_BH(_3^b)</td>
<td>+20.5</td>
<td>93</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH(_3)_BH(_3)</td>
<td>+23.8</td>
<td>91</td>
<td></td>
<td></td>
</tr>
<tr>
<td>((CH_3)_3PBH_3^c)</td>
<td>+23.8</td>
<td>91</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[{(CH_3)_2NH}_2BH_2BH_4^d]</td>
<td>+38.4</td>
<td>95</td>
<td>62</td>
<td>THF</td>
</tr>
<tr>
<td>((CH_3NH_2)_2BH_2BH_4^d)</td>
<td>+40.5</td>
<td>82</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,2-Tetramethyl-enediborane</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>+2N(CH(_3)_3</td>
<td>+1.4</td>
<td>92</td>
<td>THF</td>
<td></td>
</tr>
<tr>
<td>+2NH(CH(_3)_2</td>
<td>+6.7</td>
<td>89</td>
<td>CH(_2)Cl(_2)</td>
<td></td>
</tr>
<tr>
<td>+2NH(_2)_CH(_3)</td>
<td>+26.4</td>
<td>76</td>
<td>NH(_2)_CH(_3)</td>
<td></td>
</tr>
<tr>
<td>+2NH(_3)</td>
<td>+26.4</td>
<td>76</td>
<td>NH(_3)</td>
<td></td>
</tr>
<tr>
<td>+2P(CH(_3)_2</td>
<td>+26.1</td>
<td>90</td>
<td>49</td>
<td>THF</td>
</tr>
<tr>
<td>1,2-Bis(tetramethyl-ene)-diborane</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>+2N(CH(_3)_3</td>
<td>-2.0</td>
<td>88</td>
<td>Dioxane</td>
<td></td>
</tr>
<tr>
<td>+2NH(CH(_3)_2</td>
<td>+1.8</td>
<td>84</td>
<td>NH(CH(_3)_2</td>
<td></td>
</tr>
<tr>
<td>+2NH(_2)_CH(_3)</td>
<td>+5.2</td>
<td>81</td>
<td>NH(_2)_CH(_3)</td>
<td></td>
</tr>
<tr>
<td>+2NH(_3)</td>
<td>+13.1</td>
<td>74</td>
<td>CH(_3)CN</td>
<td></td>
</tr>
<tr>
<td>(cation)</td>
<td>+1.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>+2P(CH(_3)_2</td>
<td>+18.3</td>
<td>84</td>
<td>36</td>
<td>Dioxane</td>
</tr>
</tbody>
</table>

\(^a\)BF\(_3\)OEt\(_2\) standard.


Typical boron-11 nmr spectra of a symmetrical cleavage product and an unsymmetrical cleavage product of 1,2-tetramethylenediborane, the products of the \( \text{N(CH}_3\text{)}_3 \) and the \( \text{NH}_2\text{CH}_3 \) reactions, respectively, are shown in Figure 10. The spectrum of the \( \text{NH}_2\text{CH}_3 \) reaction product of 1,2-tetramethylenediborane is shown again in Figure 11 along with the spectrum of the same sample at a temperature where significant decomposition has occurred. The broad signal downfield from the signal due to the anion is probably in part due to the cationic boron of the ion. To demonstrate that decomposition product also contributes significantly to the signal, the sample was again cooled to -30°. At this temperature no broad signal had previously been observed in the sample, but after having been warmed to near room temperature, the signal persisted.

Boron-11 nmr spectra of both types of cleavage products of 1,2-bis(tetramethylene)-diborane are shown in Figure 12. The symmetrical cleavage example is the \( \text{NH}_2\text{CH}_3 \) adduct and the spectrum is a doublet. The unsymmetrical cleavage example is the \( \text{NH}_3 \) reaction product, and both the cationic and anionic boron signals are observed in the spectrum of the thermally stable material. At temperatures of approximately -25°, even though the resolution of the entire signal system suffered, the signal due to the cationic boron clearly disappeared.

The fact that the resonance signals for the cationic boron were not observed at low temperature in the nmr spectra
Figure 10. Boron-II nuclear magnetic resonance spectra of N(CH₃)_3 and NH₂CH₃ reaction products of 1,2-tetramethylenediborane.
Figure II. Boron–Il nuclear magnetic resonance spectra of NH$_2$CH$_3$ reaction product of 1,2-tetramethylenediborane at selected temperatures.
Figure 12. Boron-11 nuclear magnetic resonance spectra of \( \text{NH}_2\text{CH}_3 \) and \( \text{NH}_3 \) reaction products of 1,2-\textit{bis}(tetramethylene)-diborane.
of the products of unsymmetrical cleavage which were studied in this investigation is not without precedent. The temperature dependence of the cationic spectra indicates that nuclear quadrupole spin-lattice relaxation is responsible for the absence of a detectable signal at the lower temperatures. The first example of this phenomenon for boron-11 was observed by Shore and co-workers for the case of $\text{H}_2\text{B(NH}_2\text{CH}_3)_2^+$ (34).
III. DISCUSSION

A. Synthesis of the Organodiboranes

1. 1,2-Tetramethylenediborane

When butadiene and diborane were reacted in a 1:1 mole ratio in tetrahydrofuran, the yield of 1,2-tetramethylenediborane in the volatile portion of the reaction mixture was low, but considerable polymer was formed which yielded, upon heating to 125°, not only 1,2-tetramethylenediborane (I) but a comparable amount of 1,2-bis(tetramethylene)-diborane (II) as rearrangement products. When tetrahydrofuran is used as the solvent in systems in which diborane is a reactant, the diborane exists as complexed BH₃ since the molecule is cleaved symmetrically by tetrahydrofuran. Feeling that possibly BH₃ units play a large part in the formation of undesired polymeric materials, it was decided to employ as solvents ethers such as diethyl ether which do not cleave the

![Diagram of 1,2-Tetramethylenediborane (I) and 1,2-bis(tetramethylene)-diborane (II)]
diborane molecule. The reaction of 1,3-butadiene and a slight excess of $\text{B}_2\text{H}_6$ was allowed to proceed in these ether solvents for a period of three to seven days at temperatures ranging from 25-45°. Although the reaction gave good yields of 1,2-tetramethylenediborane in both diethyl ether and diisopropyl ether, dibutyl ether proved to be the best solvent with respect to separation of pure product from the reaction mixture by vacuum line fractionation. Yields of over 60 per cent of the product were realized in addition to a small amount of the isomer 1,2-(1-methyltrimethylene)-diborane (III) reported in the earlier gas phase work (16,17).

\[ \text{(III)} \]

A small amount of non-volatile polymeric material was also formed which yielded an additional amount of the product when heated to 125°. It should be noted that the molecule 1,2-tetramethylenediborane can be isolated both from the small amount of polymeric material produced in Bu$_2$O solvent and from the polymer produced in THF solvent. Therefore, a transannular hydrogen bridge type compound, \[ \text{ } \]
can be formed by the thermal rearrangement of the polymeric organoborane.

1,2-Tetramethylenediborane was identified by its vapor pressure at 0°, its boron-11 nmr spectrum, and its infrared spectrum (16,17). The compound is a clear, colorless liquid at room temperature.

2. 1,2-Bis(tetramethylene)-diborane

1,2-Bis(tetramethylene)-diborane was the major product of four reactions, each of which was performed under different conditions.

A 2:1 mole ratio of 1,3-butadiene and diborane was allowed to react at room temperature for several hours. The expected polymeric organoborane was formed. Upon heating the material to 120°, a clear, colorless liquid was liberated. In a second reaction, a 1:1 mole ratio of 1,2-tetramethylene-diborane and butadiene was allowed to react in tetrahydrofuran at 40° for two days. No polymeric material such as appeared in the first reaction was formed. Instead, there was produced a clear, colorless liquid which appeared to be identical to the thermal rearrangement product which was obtained in the first reaction. Both materials had vapor pressures of approximately 1 mm. at 25° and distilled very slowly in vacuo. Their mass spectra were identical, with the parent mass being 136 in each case. Both materials had a bridge hydrogen stretching frequency at 1614 cm⁻¹ and the
boron-11 nmr spectrum of each compound showed a chemical shift value of -28.5 ppm with respect to BF₃OEt₂. Boron-hydrogen spin coupling was not observed in the spectrum because of line broadening. The materials are evidently the same and also identical to the product which was originally isolated by Köster (14). The solution infrared spectrum shown in Figure 9 for the material prepared in this study appears to be identical to the spectrum which Köster reports for his "bis-boracyclopentane" (13). The two spectra are reproduced together in Figure 13. Since the product can be obtained at moderate temperature from the reaction of 1,2-tetramethylenediborane, a compound which has a trans-annular bridge system, and butadiene, it is suggested that probably bis-boracyclopentane is actually 1,2-bis(tetramethylene)- diborane.

\[
2 \text{1,3-C}_4\text{H}_6 + \text{B}_2\text{H}_6 \xrightarrow{\text{THF, 25°}} \text{polymer} \xrightarrow{120°} \]

\[
\text{THP polymer}
\]
Figure 13. Infrared spectra of "bis-boracyclopentane" and \textit{1,2-bis(tetramethylene)}-diborane.
1,2-**Bis**(tetramethylene)-diborane was also produced in a reaction involving a 1:1 mole ratio of butadiene and diborane as previously discussed in the synthesis of 1,2-tetramethylenediborane. The product was produced in a fourth reaction involving a 2:1 mole ratio of butadiene and diborane in diisopropyl ether at 40° for several days, the reaction conditions being those which produced 1,2-tetramethylenediborane when a 1:1 mole ratio of reactants was employed. After removal of the solvent at 0°, the product was distilled directly from the reaction vessel at 40°.

Through an equilibration reaction of his so-called "bis-boracyclopentane" with diborane, Köster has claimed to have prepared boracyclopentane-borane (13,41,42). This experiment has not been repeated in this laboratory because Köster gives no experimental details other than temperature for the equilibration; however, a comparison of the published infrared spectrum of Köster's compound,
shows that they are essentially identical as shown in Figure 14. It is well known that "In diboranes having two terminal hydrogens bound to a boron, one observes a doublet due to in-phase asymmetrical and out-of-phase symmetrical stretches" (48). Thus if the structure Köster reports were correct, the terminal boron-hydrogen stretching region would most likely be a doublet. On the other hand the singlet terminal boron-hydrogen stretching frequency favors the structure of 1,2-tetramethylenediborane. From this evidence, it is believed that the structure Köster has assigned is incorrect and that the compound is indeed 1,2-tetramethylenediborane.

The major piece of evidence toward the elucidation of the structure of the 2:1 addition product of butadiene and diborane comes from molecular weight studies. Consider the symmetrical cleavage reactions of Lewis bases with the molecule in question.

\[
\textbf{(A)} \ 
\begin{array}{c}
\text{H} \\
\text{B} \\
\text{H} \\
\text{B} \\
\text{H} \\
\text{B} \\
\text{H} \\
\text{B} \\
\end{array} 
+ 2 \text{L} \rightarrow \text{2 } \begin{array}{c}
\text{H} \\
\text{B} \\
\text{H} \\
\text{L} \\
\end{array} 
\]

\[
\textbf{(B)} \ 
\begin{array}{c}
\text{H} \\
\text{B} \\
\text{H} \\
\text{B} \\
\text{H} \\
\text{B} \\
\text{H} \\
\text{B} \\
\end{array} 
+ 2\text{L} \rightarrow \text{LBH } \begin{array}{c}
\text{B} \\
\text{H} \\
\end{array} 
\]
Figure 14. Infrared spectra of "boracyclopentane - borane" and 1,2-tetramethylenediborane.
The calculated molecular weights of the resulting products are twice as great in the case of 1,2-
$t$-bis(tetramethylene)-diborane as in the case of bis-boracyclopentane. The results of the molecular weight studies of the $N(CH_3)_3$, $NH(CH_3)_2$, and $NH_2CH_3$ reaction products are shown in Table 7.

### TABLE 7

**MOLECULAR WEIGHT DATA FROM DIOXANE SOLUTIONS**

<table>
<thead>
<tr>
<th>Amine Reactant</th>
<th>Theoretical Molecular Weight (A)</th>
<th>Experimental Molecular Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N(CH_3)_3$</td>
<td>127</td>
<td>212, 233</td>
</tr>
<tr>
<td>$NH(CH_3)_2$</td>
<td>113</td>
<td>218, 222</td>
</tr>
<tr>
<td>$NH_2CH_3$</td>
<td>99</td>
<td>208</td>
</tr>
</tbody>
</table>

The molecular weights obtained for the three adducts from dioxane solutions can only be interpreted to mean that the parent organodiborane reactant was 1,2-
$t$-bis(tetramethylene)-diborane and not bis-boracyclopentane. The values obtained for the $N(CH_3)_3$ adduct were distorted by apparent partial dissociation of the molecule in the dioxane solution.

Köster has provided some details of the derivative chemistry of 1,2-
$t$-bis(tetramethylene)-diborane which suggest that it is bis-boracyclopentane (41). The results from reactions of the compound with ammonia, primary amines, and secondary amines at temperatures where hydrogen is split out to form an aminoborane have led Köster to assign the structure
of \textit{bis-boracyclopentane} to the molecule. For example, excess diethylamine was reacted at $100^\circ$ for three hours with the organodiborane. Hydrogen was evolved quantitatively during the reaction. The molecular weight obtained from mass spectrometry measurements on the major reaction product agreed with the compound 1-diethylaminoborolane, which would seem to point to \textit{bis-boracyclopentane} as one of the original reactants. Perhaps the principle point to be made against Köster's work is that he prepared derivatives at relatively elevated temperatures, thereby increasing the probability for rearrangement reactions.

B. Reactions of the Organodiboranes

1. 1,2-Tetramethylenediborane

From the reactions of 1,2-tetramethylenediborane and selected Lewis bases, five new compounds were prepared and characterized. In the cases where the Lewis bases employed were $N(\text{CH}_3)_3$, $P(\text{CH}_3)_3$, and $NH(\text{CH}_3)_2$, the resulting products were those involving symmetrical cleavage of the hydrogen bridge system. No evidence for any unsymmetrical cleavage product was observed for the $NH(\text{CH}_3)_2$ system as might have been expected from similar work done on diborane (34). These products were stable solids which showed no tendency toward dissociation in solution or in the solid state. The trimethylamine adduct could be sublimed at $100^\circ$ quantitatively, and the dimethylamine adduct showed no tendency to split out hydrogen at temperatures up to $70^\circ$. 
On the other hand, when NH$_2$CH$_3$ and NH$_3$ were reacted with the organodiborane, unsymmetrical cleavage products which are unique examples of inorganic Zwitter ions resulted. No evidence for any symmetrical cleavage product was observed in the NH$_2$CH$_3$ system. These unsymmetrical cleavage products were found to decompose at temperatures above about -20° with the evolution of hydrogen.

The results of this cleavage study parallel the B$_2$H$_6$ system with respect to the type of cleavage product observed with each amine in that increasing methyl substitution diminished the tendency to cleave the bridge system unsymmetrically (34).

The products of the cleavage reactions were identified by their boron-11 nmr spectra. The data gathered from these spectra are shown in Table 8.
### TABLE 8
BORON-11 NUCLEAR MAGNETIC RESONANCE DATA

<table>
<thead>
<tr>
<th>Compound</th>
<th>δ (ppm)</th>
<th>J(_{BH}) (cps)</th>
<th>J(_{PB}) (cps)</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{CH}_3)_3\text{N}) adduct of 1,2-TMDB(^b) ((\text{CH}_3)_3\text{P}) adduct of 1,2-TMDB</td>
<td>+1.4</td>
<td>92</td>
<td></td>
<td>THF</td>
</tr>
<tr>
<td>((\text{CH}_3)_2\text{NH}) adduct of 1,2-TMDB</td>
<td>+26.1</td>
<td>90</td>
<td>49</td>
<td>THF</td>
</tr>
<tr>
<td>((\text{NH}_3)_2\text{BH} \text{ BH}_3)</td>
<td>+26.4</td>
<td>76</td>
<td></td>
<td>\text{CH}_3\text{NH}_2</td>
</tr>
<tr>
<td>((\text{NH}_3)_2\text{BH} \text{ BH}_3)</td>
<td>+26.4</td>
<td>76</td>
<td></td>
<td>\text{NH}_3</td>
</tr>
</tbody>
</table>

\(^{a}\)\text{BF}_3\text{OEt}_2\) standard.

\(^{b}\)1,2-TMDB = 1,2-tetramethylenediborane.

The boron-11 nmr spectra of the products of symmetrical cleavage were obtained at ambient temperature, although in the case of the NH\((\text{CH}_3)_2\) adduct, a better resolved spectrum was obtained at higher temperatures. Each spectrum consisted of a 1:2:1 triplet which resulted from spin coupling of BH\(_2\) hydrogen with boron. In the case of the P\((\text{CH}_3)_3\) adduct, each component of the triplet was split into a doublet due to spin coupling of phosphorus with boron.
The boron-11 nmr spectra of the unsymmetrical cleavage products were obtained at temperatures below -20° because of the instability of these compounds above this temperature. Each spectrum showed a 1:3:3:1 quartet which arose from spin coupling of the BH$_3$ hydrogen with boron in the anionic end of the Zwitter ion. No signal was observed for the cationic boron as might be expected from the work of Shore, Hickam, and Cowles who showed that temperatures near 30° were necessary to observe the signal of the cation when diborane is cleaved unsymmetrically by CH$_3$NH$_2$ (34). These authors indicated that nuclear quadrupole spin-lattice relaxation was responsible for the absence of a detectable triplet at low temperature in the case of the H$_2$B(NH$_2$CH$_3$)$_2^+$ cation. Additional precedent for unobserved spectra of unsymmetrical cleavage products at low temperature is given in the work of McAchran and Shore (38) and Schaeffer, Tebbe, and Phillips (49).

The chemical shifts for the compounds reported in Table 8 occur throughout at lower field than their diborane counterparts because of alkyl substitution on the boron. Generally, smaller values for the coupling constants are observed also. Certain trends are observed in the nmr data for the amine adducts of diborane. As shown in Table 5 of the experimental section, the chemical shifts for the BH$_3$ adducts increase as in the following sequence:

\[
\text{NH}_3 > \text{NH}_2\text{CH}_3 > \text{NH(CH}_3\text{)}_2 > \text{N(CH}_3\text{)}_3
\]
Heitsch reports that chemical shifts for the adducts of B(CH₃)₃ also increase according to this same sequence (50). On the other hand, the BH coupling constants in the BH₃ adducts increase according to the reverse of this sequence. From Table 8 it is seen that the two adducts of 1,2-tetramethylenediborane show the same trends in chemical shift and coupling constant values.

Unlike diborane, 1,2-tetramethylenediborane is not cleaved by tetrahydrofuran. The principal reason for this is probably the dissociative instability of the cleavage products which are formed although the possibility of a greater energy of formation for the hydrogen bridge cannot be ruled out. In all other reactions in which cleavage did indeed occur, the reactions appeared to be complete in a matter of minutes.

2. 1,2-Bis(tetramethylene)-diborane

As expected 1,2-bis(tetramethylene)-diborane also showed no tendency to react with tetrahydrofuran. It was cleaved symmetrically not only by N(CH₃)₃ and NH(CH₃)₂ but also by NH₂CH₃. No evidence for any unsymmetrical product formation was observed in the last case. This fact is possibly alarming in light of the unsymmetrical cleavage route observed for NH₂CH₃ with B₂H₆ and 1,2-tetramethylenediborane.

Reaction of 1,2-bis(tetramethylene)-diborane with ammonia produces the unsymmetrical cleavage product. Unlike the thermally unstable unsymmetrical cleavage products of
1,2-tetramethylenediborane, this product was found to be stable at 30° and showed no tendency to give off hydrogen. No evidence of symmetrical cleavage was observed.

The products of the cleavage reactions were again identified by their boron-11 nmr spectra, and the data obtained from these spectra are shown in Table 9.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta$ (ppm)</th>
<th>$J_{BH}$ (cps)</th>
<th>$J_{PB}$ (cps)</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH$_3$)$_3$N adduct of 1,2-BTMDB$^b$</td>
<td>-2.0</td>
<td>88</td>
<td></td>
<td>Dioxane</td>
</tr>
<tr>
<td>(CH$_3$)$_3$P adduct of 1,2-BTMDB</td>
<td>+18.3</td>
<td>84</td>
<td>36</td>
<td>Dioxane</td>
</tr>
<tr>
<td>(CH$_3$)$_2$NH adduct of 1,2-BTMDB</td>
<td>+1.8</td>
<td>84</td>
<td></td>
<td>NH(CH$_3$)$_2$</td>
</tr>
<tr>
<td>CH$_3$NH$_2$ adduct of 1,2-BTMDB</td>
<td>+5.2</td>
<td>81</td>
<td></td>
<td>NH$_2$CH$_3$</td>
</tr>
<tr>
<td>(NH$_3$)$_2$B$_2$H$_2$</td>
<td>+13.1</td>
<td>74</td>
<td></td>
<td>CH$_3$CN</td>
</tr>
<tr>
<td></td>
<td>+1.6 (cat.)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$BF$_3$OEt$_2$ standard.

$^b$1,2-BTMDB = 1,2-bis(tetramethylene)-diborane.

All spectra were obtained at ambient temperature. Each spectrum of the symmetrical cleavage products consisted
of a doublet except in the case of the \((\text{CH}_3)_3\text{P}\) adduct where 
P-B coupling complicated the spectrum. When the spectrum of 
the \((\text{CH}_3)_3\text{P}\) adduct was obtained at higher temperatures, only 
coupling due to BH hydrogen was observed, indicating, per­
haps, that there is rapid exchange of the ligand molecules 
at the boron site at these temperatures.

The spectrum of the unsymmetrical cleavage product of 
the \(\text{NH}_3\) reaction showed both the 1:2:1 triplet of the anionic 
boron and the singlet of the cationic boron at 30°.

The trends discussed earlier concerning chemical 
shifts and coupling constants are followed consistently in 
the \(1,2\text{-bis-}(\text{tetramethylene})\)-diborane system as shown in 
Table 9.

The relative yields of symmetrical and unsymmetrical 
cleavage products of the reactions of diborane and the two 
organodiboranes prepared in this study with amine bases are 
presented in Table 10.

It appears that a general rule might now be expanded. 
Although factors which determine whether a Lewis base will 
produce symmetrical or unsymmetrical cleavage are still not 
understood, steric factors certainly play an important role. 
The tendency to cleave the hydrogen bridge system unsym­
metrically in the diborane compounds studied diminishes with 
increased alkyl substitution on both the amine and the 
diborane. Thus in the case of \(\text{B}_2\text{H}_6\), the only amine base 
which will cleave the bridge system exclusively in
<table>
<thead>
<tr>
<th>Reactants</th>
<th>Unsymmetrical Cleavage Product</th>
<th>Relative Yield</th>
<th>Symmetrical Cleavage Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_2H_6 + 2NH_3$</td>
<td>$[BH_2(NH_3)_2]^+[BH_4^-]$</td>
<td>No evidence</td>
<td>$CH_3NH_2BH_3$</td>
</tr>
<tr>
<td>+ $2NH_2CH_3$</td>
<td>$[BH_2(NH_2CH_3)_2]^+[BH_4^-]$</td>
<td>$\gg$</td>
<td>$CH_3NH_2BH_3$</td>
</tr>
<tr>
<td>+ $2NH(CH_3)_2$</td>
<td>$[BH_2(NH(CH_3)_2)_2]^+[BH_4^-]$</td>
<td>$&lt;$</td>
<td>$(CH_3)_2NHBH_3$</td>
</tr>
<tr>
<td>+ $2N(CH_3)_3$</td>
<td>No evidence for product</td>
<td></td>
<td>$(CH_3)_3NBH_3$</td>
</tr>
</tbody>
</table>

Diagram:

- $B_2H_6 + 2NH_3$ to $[BH_2(NH_3)_2]^+[BH_4^-]$
- $2NH_2CH_3$ to $[BH_2(NH_2CH_3)_2]^+[BH_4^-]$
- $2NH(CH_3)_2$ to $[BH_2(NH(CH_3)_2)_2]^+[BH_4^-]$
- $2N(CH_3)_3$ to $[BH_2(NH(CH_3)_2)_2]^+[BH_4^-]$
TABLE 10 (continued)

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Unsymmetrical Cleavage Product</th>
<th>Relative Yield</th>
<th>Symmetrical Cleavage Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>+ 2NH₃</td>
<td>(NH₃)₂B⁺BH₂</td>
<td>No evidence for product</td>
<td></td>
</tr>
<tr>
<td>+ 2NH₂CH₃</td>
<td>No evidence for product</td>
<td></td>
<td></td>
</tr>
<tr>
<td>+ 2NH(CH₃)₂</td>
<td>No evidence for product</td>
<td></td>
<td></td>
</tr>
<tr>
<td>+ 2N(CH₃)₃</td>
<td>No evidence for product</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

No evidence for product
symmetrical fashion is \((\text{CH}_3)_3\text{N}\); in the case of 1,2-tetramethylenediborane a less hindered base, \((\text{CH}_3)_2\text{NH}\), will cleave the bridge system symmetrically; and in the case of 1,2-bis(tetramethylene)-diborane an even less hindered base, \(\text{CH}_3\text{NH}_2\), will cleave the bridge system symmetrically.

As discussed in the introduction, there is evidence that the cleavage of the hydrogen bridge system takes place in stepwise fashion. It has been suggested that the first step involves the rupture of one hydrogen-bridge bond,

\[
\text{H}_3\text{B}-\text{H}-\text{BH}_3 + L \rightarrow \text{H}_2\text{B}-\text{H}-\text{BH}_3\]

while the second step involves rupture of the second bridge bond, with the point of attack determining whether the cleavage is symmetrical or unsymmetrical \((30,32)\).

\[
\text{H}_2\text{B}-\text{H}-\text{BH}_3 + L \rightarrow \text{H}_2\text{BL}_2\text{BH}_4 \quad \text{unsymmetrical}
\]

In general, it appeared that reactions occurred more slowly in the systems where 1,2-bis(tetramethylene)-diborane was a reactant. There was also evidence that the \((\text{CH}_3)_3\text{N}\) adduct was partially dissociated at room temperature, implying a less stable adduct than the \((\text{CH}_3)_3\text{N}\) adducts of
diborane and 1,2-tetramethylenediborane. The fact that the 
(CH₃)₂NH and NH₂CH₃ adducts exhibited no such dissociation 
at room temperature shows that steric factors are in opera­
tion in the reactions. The results of this study generally 
parallel those results obtained by Brown for B(CH₃)₃ with 
the methyl-substituted amine series (51).

The reaction rate with respect to cleavage of the 
bridge system apparently decreases according to the 
following sequence:

\[
\text{B}_2\text{H}_6 \quad \text{\textgreater} \quad \text{H}_\text{H}_\text{H}_\text{H} \quad \text{\textgreater} \quad \text{H}_\text{H}_\text{H}_\text{H}
\]

This fact might possibly account for the observation that, 
contrary to the diborane case, the cleavage products in the 
other two cases appeared to be totally one type in the reac­
tion of a particular base. It is possible that in the 
slower reactions, the type of cleavage product is determined 
by thermodynamic and not kinetic effects. This would 
account for the absence of a symmetrical product in the 
reaction of NH₂CH₃ with 1,2-tetramethylenediborane and in the 
reaction of NH₃ with 1,2-bis(tetramethylene)-diborane when 
such a product might be expected to be present in significant 
amounts.
BIBLIOGRAPHY


7. E. Krause and R. Nitsche, Ber., 54, 2784 (1921).


45. R. T. Sanderson, "Vacuum Manipulation of Colatibe Com-


