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<u>ROGER KARVEL HEUSSER</u>   for the   <u>MASTER OF SCIENCE</u>
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Title: <u>PREPARATION AND CHARACTERIZATION OF   </u>

<u>N-OCTADECYLCYCLOAZADIBORON   </u>

Abstract approved: <u>   </u>
                            T. D. Parsons

A preparative method for a new compound n-octadecylcycloazadi-boron (CAB), in high yield has been developed. CAB was isolated as an intermediate in the octadecylamine-catalyzed hydrolysis of penta-borane. The most probable structure of CAB can be regarded as a derivative of the three membered ring cycloazadiboron with a n-octadecyl group substituted for hydrogen on nitrogen. For each mmole of CAB reacted in vacuo with 2 mmole of anhydrous hydrogen chloride 1 mmole of hydrogen gas is obtained. CAB was established to add 1 mmole of boron trichloride per mmole reacted at $0^{\circ}C$ in vacuo to form the Lewis acid-base adduct. Cyclohexene was reduced by addition (1:1) to CAB. Subsequent reaction with acetic acid gave cyclohexane and hydrogen gas. The infrared spectrum of CAB was obtained. Acid hydrolysis of CAB provides 2 mmole of hydrogen per mmole reacted. The chemical characterization of the compound

strongly indicates the proposed structure as opposed to other struc-

tures considered.

Preparation and Characterization of N-Octadecylcycloazadiboron

by

Roger Karvel Heusser

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_____

Associate Professor of Chemistry
                 in charge of major

_____

Chairman of Department of Chemistry

_____

Dean of Graduate School

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INTRODUCTION

Nature of the Boron Hydrides

Interest in the chemistry of the boron hydrides dates from the early part of this century when Alfred Stock (98) first prepared and characterized a series of such hydrides produced by the acid hydrolysis of magnesium boride. These included diborane, B_2H_6, tetraborane, B_4H_{10}, pentaborane-9, B_5H_9, pentaborane-11, B_5H_{11}, hexaborane, B_6H_{10}, and decaborane, $B_{10}H_{14}$. Improved syntheses of all of these hydrides have been developed over the years and several others have been discovered. Pentaborane-9, which is of particular interest in this work, was prepared in larger quantities by Schlesinger and Burg (89) by the reaction of diborane and anhydrous hydrogen chloride. Now, higher hydrides are prepared from diborane by thermal cracking reactions (87).

The structures of the boron hydrides have been determined by a variety of experimental methods. These structures and the experimental means of their determination have been reviewed by Lipscomb (62). For most of these molecules the arrangement of boron atoms corresponds to the arrangement of points on the surface of an icosahedron (Figure 1). These include tetraborane, pentaborane-11,
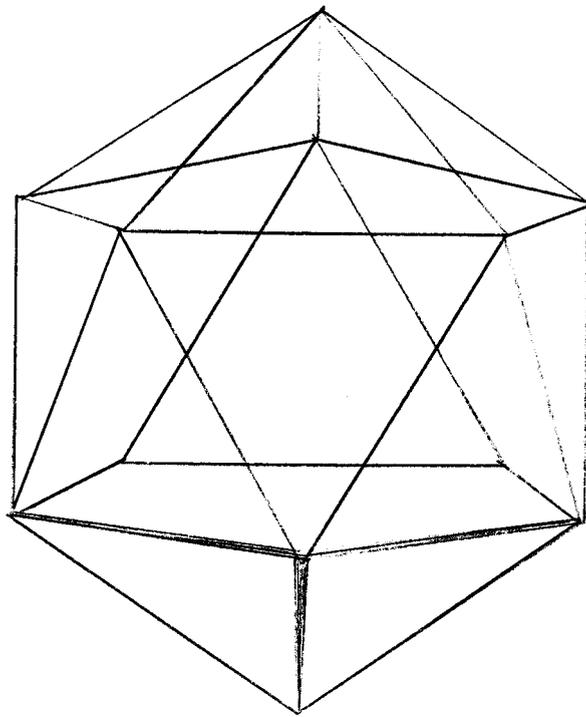
Figure 1. Icosahedron Structure

hexaborane and decaborane among those listed earlier. Pentaborane-9 is the only known exception, having a square pyramidal arrangement of boron atoms. Its structure, including hydrogens is given in Figure 2.

Dulmage and Lipscomb (28, 29, 65) established the pentaborane molecule to have a pyramidal structure of molecular symmetry C_{4v} by x-ray diffraction methods. A similar structure was found for gaseous pentaborane by electron diffraction methods (45, 46, 47) and by microwave, raman and infrared spectroscopy studies (52, 53, 54, 99). The mass spectrum of pentaborane shows a fragmentation pattern that can be correlated with this structure (81). Four boron atoms form the base of the pyramid with a single hydrogen bridge between each pair of boron atoms. The four base boron atoms are connected to an apical boron which forms the top of the pyramid. Each boron atom in pentaborane is bonded to a terminal hydrogen by a single bond. Thus of the total of nine hydrogens in pentaborane four are in bridge positions and five are singly bonded to boron, one per boron atom. The boron-boron bond arrangement is very similar to the octahedral structure of the cubic metal borides (Figure 3). Removing one boron atom from the octahedron and adding four hydrogen bonds to the open face between borons and attaching one terminal hydrogen atom to each boron generates the structure of stable pentaborane (65, 96).

$B_1 - B_2 = 1.66 \ \overset{\cdot}{A}$

$B_2 - B_2 = 1.77 \ \overset{\cdot}{A}$

$B_1 - H_1 = 1.21 \ \overset{\cdot}{A}$

$B_2 - H_3 = 1.35 \ \overset{\cdot}{A}$

$B_2 - H_2 = 1.21 \ \overset{\cdot}{A}$
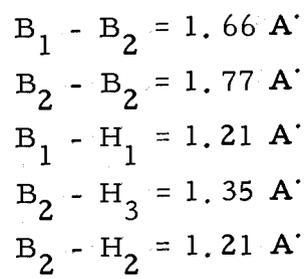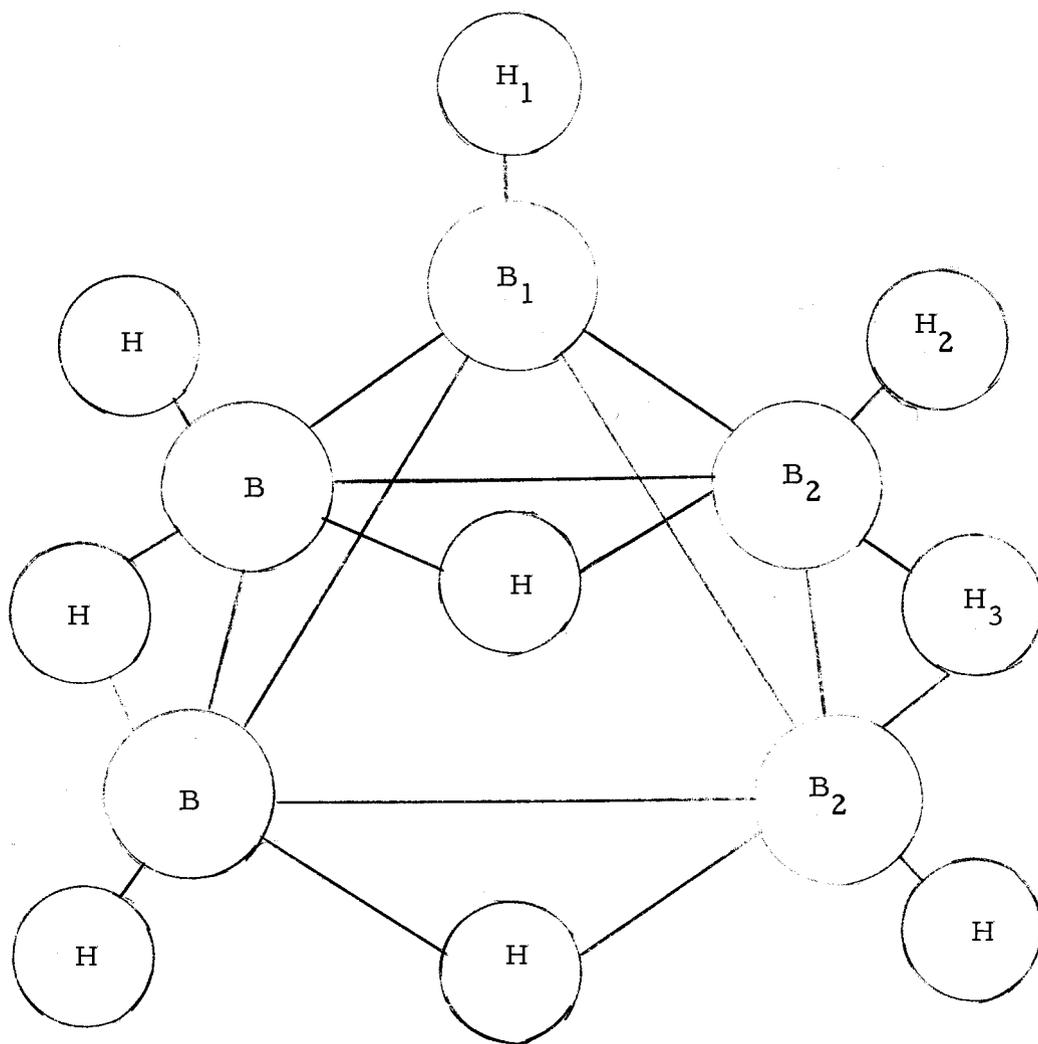
Figure 2. Structure of Pentaborane
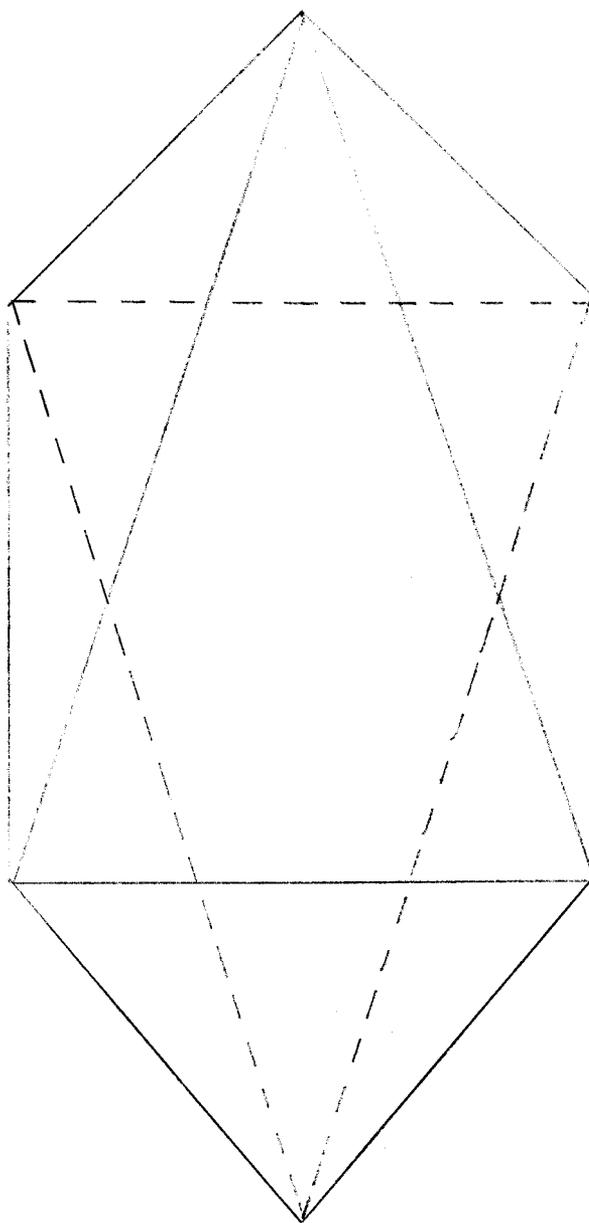
Figure 3. Octahedron Structure

A basic molecular orbital or directed valence bond treatment of pentaborane in terms of three center bonds predicts a negative formal charge of -1 on the apex boron atom and a small positive formal charge of + 1/4 on each of the four base boron atoms of pentaborane (20, 27, 30, 49, 62, 63, 85). For convenience the topological model of pentaborane-9 suggested by Lipscomb (62) will be used in this thesis.
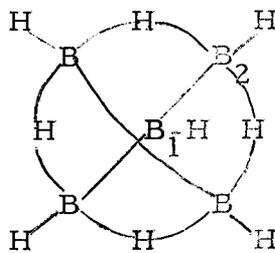
A.

Normal two-center bonds are shown in the usual ways, B-H or B-B; three center bonds are represented by

Substitution and Addition Reactions of Pentaborane

In the past decade a number of studies have given some insight into the modes of reaction of pentaborane-9 with a variety of reagents. Many of these involve substitution reactions of one or more attached hydrogen atoms without rearrangement or destruction of the boron framework. In general, the position of addition or substitution on the boron framework confirms the molecular polarity given by molecular

orbital calculations.

A general reaction of boron hydrides is the hydroboration of olefins (10, 11, 12). This reaction gives addition of B-H to double bonds of olefins. For example, diborane reacts with cyclohexene to give tris-cyclohexylborane.

$$3C_6H_{10} + 1/2\,B_2H_6 \longrightarrow (C_6H_{11})_3B$$
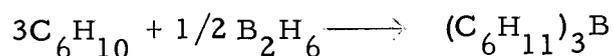
Nucleophilic attack by an olefin on pentaborane was expected and established to occur at the point of lowest electron density in the boron framework, at a base boron atom. Ryschkewitsch (85) reacted various olefins at 150°C with pentaborane obtaining alkyl derivatives of pentaborane with substitution at the base atom.

$$B_5H_9 + RCH=CH_2 \xrightarrow{\ 150°C\ } 2\text{-}B_5H_8CH_2CH_2R$$
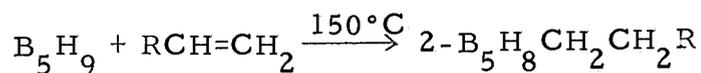
Blay (9) in separate work established ethylated polymers of pentaborane of the form $(B_5H_{9-n})(Et)_n$ where n equals one to three.

Friedel-Crafts ethylation of pentaborane or other electrophilic substitutions would be expected to take place at the region of high electron density, the apical position. Substitution at this position has been confirmed by the reaction of olefins or alkyl halides with pentaborane-9 in the presence of Lewis acids. Multiple alkylation of pentaborane does not occur under the conditions of Friedel-Crafts reactions even under drastic conditions (1, 8, 34, 68, 75, 84).

Figgis and Williams (31) confirmed the structure of ethylpentaborane

prepared by a Friedel-Crafts reaction. The ethyl group was found

to be located at the apical position of the pentaborane molecule.

$$B_5H_9 + CH_3CH_2I \xrightarrow{\text{AlCl}_3} 1\text{-}CH_3CH_2B_5H_8 + HI$$
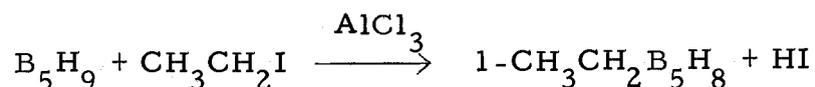
In the absence of a strong Lewis acid the chlorination of

pentaborane is a radical reaction which takes place one hundred times

faster when irradiated with strong ultraviolet light and gives substitu-

tion at a basal boron. In contrast, chlorination in the presence of a

Lewis acid gives apical substituted halopentaboranes almost

exclusively and in high yields. These latter reactions are considered

to be electrophilic substitutions (34, 43, 88, 95).

$$B_5H_9 + Cl_2 \longrightarrow 2\text{-}ClB_5H_8 + HCl$$

$$B_5H_9 + Cl_2 \xrightarrow{\text{AlCl}_3} 1\text{-}ClB_5H_8 + HCl$$

$$B_5H_9 + Br_2 \longrightarrow 1\text{-}BrB_5H_8 + HBr$$
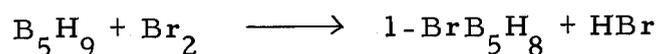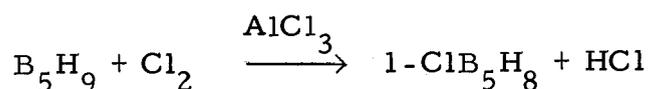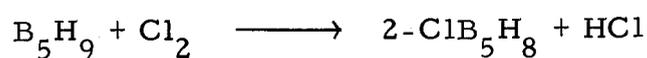
T. Onak (68) suggested that the position of substitution on

pentaborane is kinetically rather than thermodynamically controlled,

since basal-substituted alkyl-pentaboranes are found to be about 3

kilocalories per mole more stable than the corresponding apical

substituted pentaboranes. This is confirmed by the rearrangement

of 1-alkylpentaboranes into the 2-alkylpentaboranes in the presence
of 2,6-dimethylpyridine (64, 68, 69, 75, 84) or by heating at elevated
temperatures (71).

Burg and Sandhu (17) established the reversible conversion of
apical-substituted bromopentaborane to basal-substituted bromo-
pentaborane to be catalyzed by hexamethylenetetramine. Onak and
Dunks (70) established the first halogen exchange in a polyborane by
heating 1-bromopentaborane with aluminum trichloride providing a
small yield of 2-chloropentaborane.

Burg (14) later developed a minimal pressure gas flow process
which provides a high yield of halogen exchange of the monohalo-
pentaborane derivatives at the same position. Using the gas flow
process and mercuric chloride as a catalyst 1-iodopentaborane pro-
vides 1-chloropentaborane. Antimony trifluoride catalyzes the
exchanges of 2-iodopentaborane to a recently isolated compound 2-
fluoropentaborane. Apical substituted halogen pentaboranes of the
type $1\text{-}XB_5H_8$ are more stable when X is a heavier halogen. Basal
substituted halogen pentaboranes of the type $2\text{-}XB_5H_8$ are more stable
when X is a low molecular weight halogen.

The cis dimethyl dibasal-substituted pentaborane was prepared
by rearrangement from the 1,2-dimethyl pentaborane in the presence
of 2,6-dimethylpyridine (2,6-DMP) and confirmed by an x-ray
diffraction study (32, 64, 76). The $1,2\text{-}(CH_3)_2B_5H_7$ used was

produced by Friedel-Crafts methylation of 2-methylpentaborane.

Hough and co-workers (50) observed the isomerization of 1-ethylpentaboranes in the presence of trimethylamine to 2-ethyl-pentaboranes. The trimethylammonium ethylhydriopentaborate, $(CH_3)_3NHB_5H_7C_2H_5$, salt was isolated and is stable below 28°C. When the salt, $(CH_3)_3NHB_5H_7C_2H_5$, is heated above its dissocation temperature (28°C) 2-ethylpentaborane is recovered. The isolation of the trimethylammonium ethylhydriopentaborate is evidence for the ethylhydriopentaborate ion $(B_5H_7C_2H_5^-)$ being the key intermediate for the isomerization.

$$1-C_2H_5B_5H_8 \xrightarrow{N(CH_3)_3} 2-C_2H_5B_5H_8$$
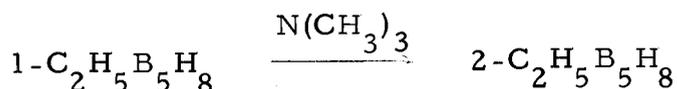
Treatment of pentaborane with deuterium chloride in the presence of aluminum trichloride results in the rapid exchange of hydrogen and deuterium in the apical position of pentaborane. The exchange studies of Onak (73) are in agreement with the fact the apical position of pentaborane is the most susceptible to electrophilic attack. Apical substituted deuteriopentaborane rapidly exchanges with all hydrogens in the presence of 2,6-dimethylpyridine (2,6-DMP). An intramolecular exchange mechanism would be expected to form only three isomers of deuteriopentaborane, B_5H_8D, (1,2- and u). As established by mass spectral data, the intramolecular

deuterium-protium exchange takes place in 1-deuteriopentaborane
when catalyzed by 2,6-DMP at room temperature. However, the
thermal rearrangement of 1-deuteriopentaborane, in the absence of
a Lewis base, provided a nearly statistical distribution of deuterio-
pentaborane products as would be expected from an intermolecular
mechanism (72).

Apical substituted deuterio and alkyl pentaboranes are stable
at room temperature, in the absence of a Lewis base. If in forming
the Lewis base adduct the apical boron becomes equivalent to any
other boron, the subsequent dissocation of the adduct will allow the
apical boron to become a basal boron. Such an unstable intermediate
might have the structure, B, which is similar to the known 2,4-
dimethylenetetraborane. When R is an alkyl group, the more thermo-
dynamically stable 2-alkyl derivative will result. Tautomerism of
hydrogens and accompanying skeletal rearrangement is characteristic
of boron hydride Lewis base adducts and an intermolecular intermedi-
ate requires only a slight amount of rearrangement (71, 72, 104).
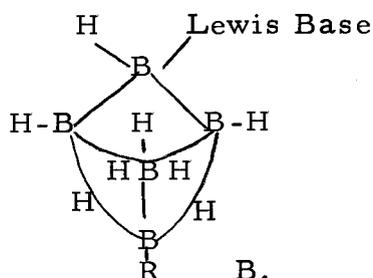
Koski and co-workers (56, 57, 58, 59, 60) established the exchange reaction of deuteriated diborane with pentaborane proceeded preferentially in the terminal positions of pentaborane. Under the experimental conditions the bridge hydrogens in pentaborane did not participate in exchange with deuterium from deuteriated diborane.

Degradation Reactions of Pentaborane-9

Pentaborane-9 can be degraded in a variety of ways giving borohydride ions or base complexes of fragments of the original structure. The simplest degradation is the loss of a proton to give the $B_5H_8^-$ ion. Gaines and co-workers (36) first produced the $B_5H_8^-$ ion by reaction of pentaborane with butyl lithium in ether solvent at low temperatures.

$$Li(n-C_4H_9) + B_5H_9 \longrightarrow n-C_4H_{10} + LiB_5H_8$$

Reaction of the salt with anhydrous hydrogen chloride regenerates pentaborane in high yield.

$$LiB_5H_8 + HCl \longrightarrow LiCl + B_5H_9$$

A similar reaction with deuterium chloride produces monodeuterio-pentaborane. Comparison of the proton nuclear magnetic resonance (NMR) spectrum of monodeuteriopentaborane with that of pentaborane indicated there was a decrease in intensity only in the bridge hydrogen

region which is evidence for the addition of deuterium to the bridge

position. The reactions are then

$$\text{Li}(n\text{-}C_4H_9) + \text{[pentaborane structure]} \longrightarrow n\text{-}C_4H_{10} + \text{Li}^+ \text{[pentaborane anion structure]}$$

$$\text{Li}^+ \text{[pentaborane anion structure]} + \text{DCl} \longrightarrow \text{LiCl} + \text{D [pentaborane structure]}$$
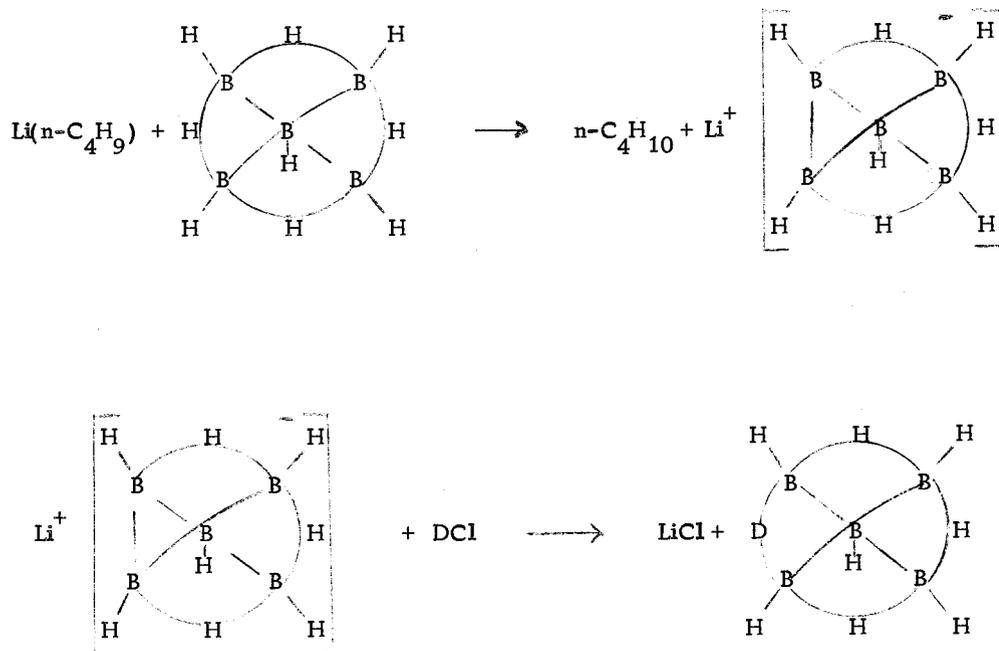
The prefix u is used to identify substitution in the bridge position,

thus u-monodeuteriopentaborane or 2,3-u-monodeuteriopentaborane.

The structure of the $B_5H_8^-$ ion and the nature of the substitution

product has been amply confirmed in a series of recent studies.

Gaines and Iorns (35, 37) prepared a new class of pentaborane

derivatives of the general formula $u\text{-}R_3M_{IV}B_5H_8$ where M_{IV} may

be silicon, germanium or tin and R is hydrogen or an alkyl group.

The M_{IV} atom occupies the bridging position between two boron atoms

in the base of the pentaborane pyramid as determined by detailed

nuclear magnetic resonance (NMR) studies. A typical M_{IV} bridging

compound can be prepared by reacting R_3SiCl with lithium

pentaborate. Isomerization of $u\text{-}R_3M_{IV}B_5H_8$ to the more volatile

$2\text{-}R_3M_{IV}B_5H_8$ compounds occurs rapidly in the presence of weak

Lewis base catalysts such as dimethyl ether.
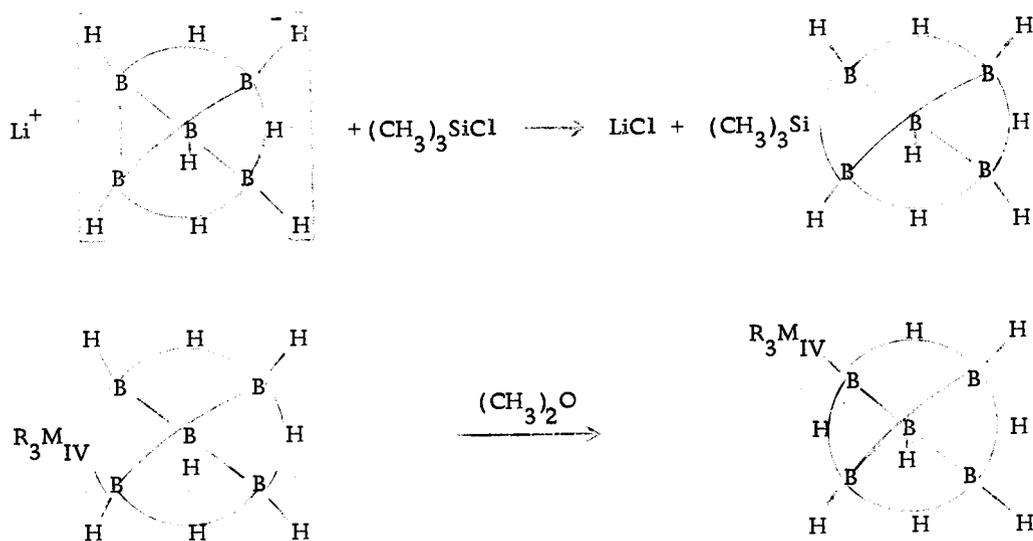
Burg and Heinen (15) prepared a similar phosphino derivative,

$2,3\text{-}u\text{-}(CH_3)_2PB_5H_8$, by reaction of lithium pentaborate with

phosphines of the type R_2PCl where R is an alkyl group. The

phosphorus atom bridges two boron atoms on the base of the penta-

borane pyramid. Phosphines of weak base strength such as

$(CF_3)_2PCl$ give substitution at the apical position of pentaborane

rather than at the bridging position.

$$(CH_3)_2PCl + LiB_5H_8 \longrightarrow LiCl + 2,3\text{-}u\text{-}(CH_3)_2PB_5H_8$$

$$(CF_3)_2PCl + LiB_5H_8 \longrightarrow LiCl + 1\text{-}(CF_3)_2PB_5H_8$$
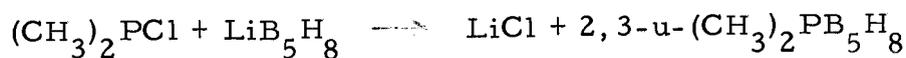
There have been several studies in which one or more borons have been removed from the pentaborane structure with the residue stabilized by complexation with a Lewis base. The simplest such reaction would be the loss of a BH_3 (borine) fragment from a basal position:

H   H   H

$B_4H_6 + BH_3$

H   H

H   H   H
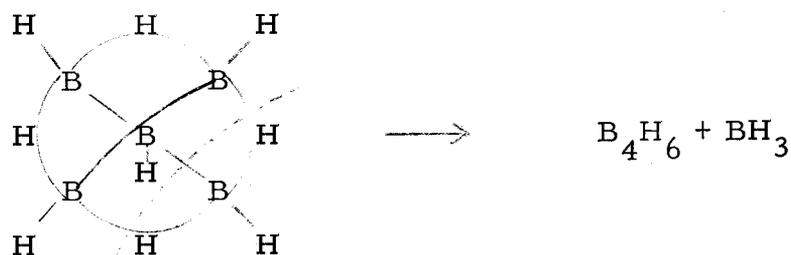
Burg (13) determined that pentaborane adds two moles of trimethylamine at low temperatures. If excess amine is left in contact with this material slow cleavage is observed with formation of trimethylamine borane and a polymer.

$$(2+X)(CH_3)_3N + B_5H_9 \longrightarrow 2(CH_3)_3N \cdot BH_3 + [B_3H_3 \cdot X(CH_3)_3N]_n$$
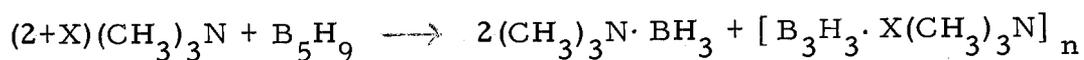
When the excess amine is not present the cleavage reaction occurred according to (13, 16, 41, 51):

$$B_5H_9 \cdot 2N(CH_3)_3 \longrightarrow (CH_3)_3NBH_3 + (CH_3)_3NB_4H_6$$

In a reaction that is formally analagous to Burgs work, pentaborane loses a BH_3 group when treated with substituted acetylenes in

the presence of 2,6-dimethylpyridine (2,6-DMP) (74).

$$B_5H_9 + RC \equiv CR' + 2,6\text{-}DMP \longrightarrow B_4H_6C_2RR' + 2,6\text{-}DMP \cdot BH_3$$

The B_4H_6 fragment may have undergone rearrangement in this case.

At room temperature pentaborane was established to add to

N,N,N',N'-tetramethylenediamine (TMED). When the addition com-

pound is reacted with methanol at 0°C one boron is removed by

alcoholysis. The diamine ligand could span two boron atoms or

chelate one boron atom (66).

$$B_5H_9 + TMED \longrightarrow B_5H_9 \cdot TMED$$

$$B_5H_9 \cdot TMED + 3CH_3OH \longrightarrow B_4H_8 \cdot TMED + B(OCH_3)_3 + 2H_2$$
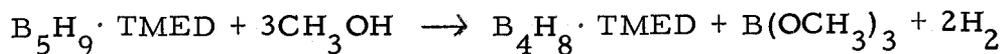
The most reasonable structure of $B_4H_8 \cdot$ TMED, on the basis of NMR

data, is one in which the diamine ligand chelates one boron. In the

probable structure, C, the TMED ligand is represented by .
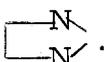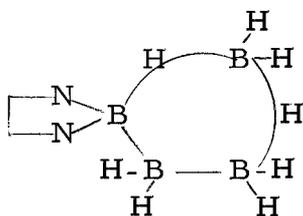
C.

The triborohydride ion, $B_3H_8^-$, ion was first isolated by

Graybill (42) as a product of the alcoholysis of tetramethylammonium

nonaborohydride.

$$(CH_3)_4NB_9H_{12} + 18CH_3OH \longrightarrow (CH_3)_4NB_3H_8 + 6B(OCH_3)_3 + 11H_2$$
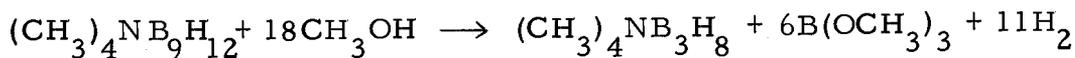
Reaction of the product, tetramethylammonium triborohydride with

trimethylamine hydrochloride gives trimethylamine triborane.

$$(CH_3)_3NHCl + (CH_3)_4NB_3H_8 \longrightarrow (CH_3)_3N \cdot B_3H_7 + H_2 + (CH_3)_4NCl$$
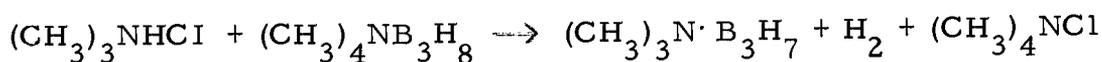
Geanogel and co-workers (39, 40) have since prepared the

triborohydride ion by degradation of pentaborane. In the process

they showed that pentaborane can be deprotonated by a variety of bases

in addition to butyl lithium which was used by Gaines in his original

work. Thus

$$NaH + B_5H_9 \longrightarrow H_2 + NaB_5H_8$$

$$NaB_5H_8 + (CH_3)_4NCl \longrightarrow NaCl + (CH_3)_4NB_5H_8$$

$$(CH_3)_4NB_5H_8 + 6 \ i\text{-}C_3H_7OH \longrightarrow (CH_3)_4NB_3H_8 + 2B(i\text{-}OC_3H_7)_3 + 3H_2$$
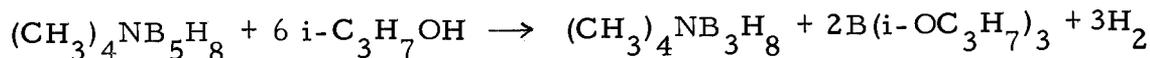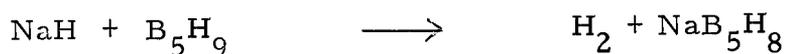
Although it has not been prepared from pentaborane, a two

boron fragment of the type $B_2H_4 \cdot 2PR_3$ has recently been isolated by

Deever and co-workers (23).

Shapiro and co-workers (83, 93) determined no boron exchange

between isotopically normal pentaborane and enriched B^{10} penta-

borane at temperatures up to 100°C in the liquid phase or up to 250°C

in the gas phase. Later research by Hillman and co-workers (41) isolated a small yield of B^{10} enriched pentaborane from exchange between B^{10} enriched diborane and isotopically normal pentaborane. Evidence indicated the rearrangement involved an exchange of two borons at a time from diborane.

Oxidation and Hydrolysis of Pentaborane-9

The oxidation of pentaborane by oxygen gas has been the subject of a number of studies. Pentaborane and oxygen explode when mixed within proper pressure and mole ratio limits. The complete oxidation of pentaborane by oxygen (19, 55) is given by the equation:

$$2B_5H_9 + 12O_2 \longrightarrow 5B_2O_3 + 9H_2O$$

Price (79) discovered a bluish light or spark to be emitted just below the first explosion limit when pentaborane is reacted with oxygen in spherical pyrex bulbs. The time dependence of the bluish light is described by $-dI/dT = KI^2$, where I is light intensity and K a constant. This constant K increases with increasing pentaborane pressure but decreases with increasing oxygen pressure. Reaction of pentaborane with oxygen is assumed to be of the branched chain type, indicated by the explosion limit. At the explosion limit the rate of chain branching must equal that of chain breaking reactions.

Baden, Bauer and Wiberley (3) reported the formation of

diborane, hydrogen and a white solid when dry air was allowed to

slowly oxidize pentaborane. The progressive disappearance of

pentaborane and the simultaneous accumulation of diborane was fol-

lowed by infrared absorption measurements. Later these same

workers isolated an intermediate compound in the partial oxidation

of pentaborane which has the formula $B_4H_{12}O$. In explosions the

products were boron trioxide, higher hydrides of the type $(BH)_x$

and water in proportions dependent upon initial mixture ratios (3, 4,

6, 7). Ditter and Shapiro (24, 25) isolated an intermediate compound

in the partial oxidation of pentaborane which has the formula $B_2H_2O_3$.

Recent separate reports by Barton and co-workers (5) and Lee and

co-workers (61) indicate that boroxine $(H_3B_3O_3)$ is formed initially

and further oxidation yields $H_2B_2O_3$ with boron trioxide being the

ultimate product. When pentaborane is reacted with enriched O^{18}

oxygen the boroxine formed contains oxygen atoms in a statistical

distribution while the oxidized product $H_2B_2O_3$ contains oxygen in a

nonstatistical distribution. This situation is suggested to arise if the

immediate precursor to boroxine were a molecule with a peroxide

structure. The chemical nature of $H_2B_2O_3$ is consistent with a

molecule having a planar structure (five membered ring with a O-O

bond). Studies of the oxidation of trialkyl boranes has provided

ample evidence for the existence of peroxide intermediates in the

oxidation of boranes by oxygen (21, 22, 44, 67, 77, 78).
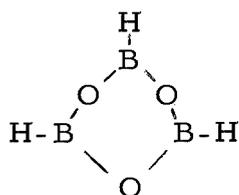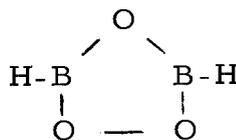
$$\text{Boroxine } H_3B_3O_3 \qquad\qquad H_2B_2O_3$$

The hydrolysis of pentaborane under a variety of conditions has been the subject of considerable research. Alfred Stock (98) reported about fifty years ago that pentaborane is the most stable of the boron hydrides in the presence of water. Pentaborane reacts very slowly with cold water and a moderate degree of hydrolysis is attained only after heating at 90°C for three days. Complete hydrolysis is represented by the equation:

$$B_5H_9 + 15H_2O \longrightarrow 5H_3BO_3 + 12H_2$$
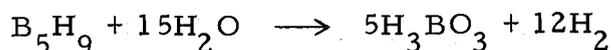
Shapiro and Weiss (93) established that the slow rate of hydrolysis can be attributed to the poor miscibility of pentaborane and water. When an inert mutually miscible solvent, such as dioxane, is used the rate of reaction becomes too rapid to measure. Shapiro and Weiss (92) proposed a removal of a borine group (BH_3) by water as the first step in the hydrolysis of pentaborane with subsequent hydrolysis of the borine group to produce hydrogen. This mechanism indicated a tetraborane (B_4H_6) skeleton left after the initial removal of a basal boron atom from the pyramidal pentaborane structure.

However, recent exchange studies cited previously provide ample evidence for the hydrolysis of pentaborane to proceed initially by the hydrolysis of the more reactive terminal hydrogens than by the destruction of the pentaborane skeleton as proposed by Shapiro and Weiss (92). It has been suggested that the oxidation reaction mechanism of pentaborane is very similar to the mechanism of hydrolysis (18).

The vapor phase hydrolysis of pentaborane was studied by Butler and co-workers (18). The reaction was initially first order with respect to pentaborane concentration. At 85°C the reaction of pentaborane with excess water was found to be very slow, but at 150°C it proceeded at a measurable rate. With excess water or a stoichiometric ratio the initial reaction rate decreased slowly until about 5 moles hydrogen per mole pentaborane had been produced (Figure 4). At this point an acceleration in the rate of hydrogen production was observed. From this data Butler and co-workers (18) proposed a mechanism consisting of initial hydrolysis of the five terminal hydrogens at a decreasing rate followed by disruption of the pyramidal boron structure and/or hydrolysis of the four bridge hydrogen atoms at an accelerated rate.

Reed and co-workers (26, 82) studied the fate of tritiated pentaborane in small animals in an attempt to elucidate the toxicity mechanism of pentaborane. They found that the hydrolysis of
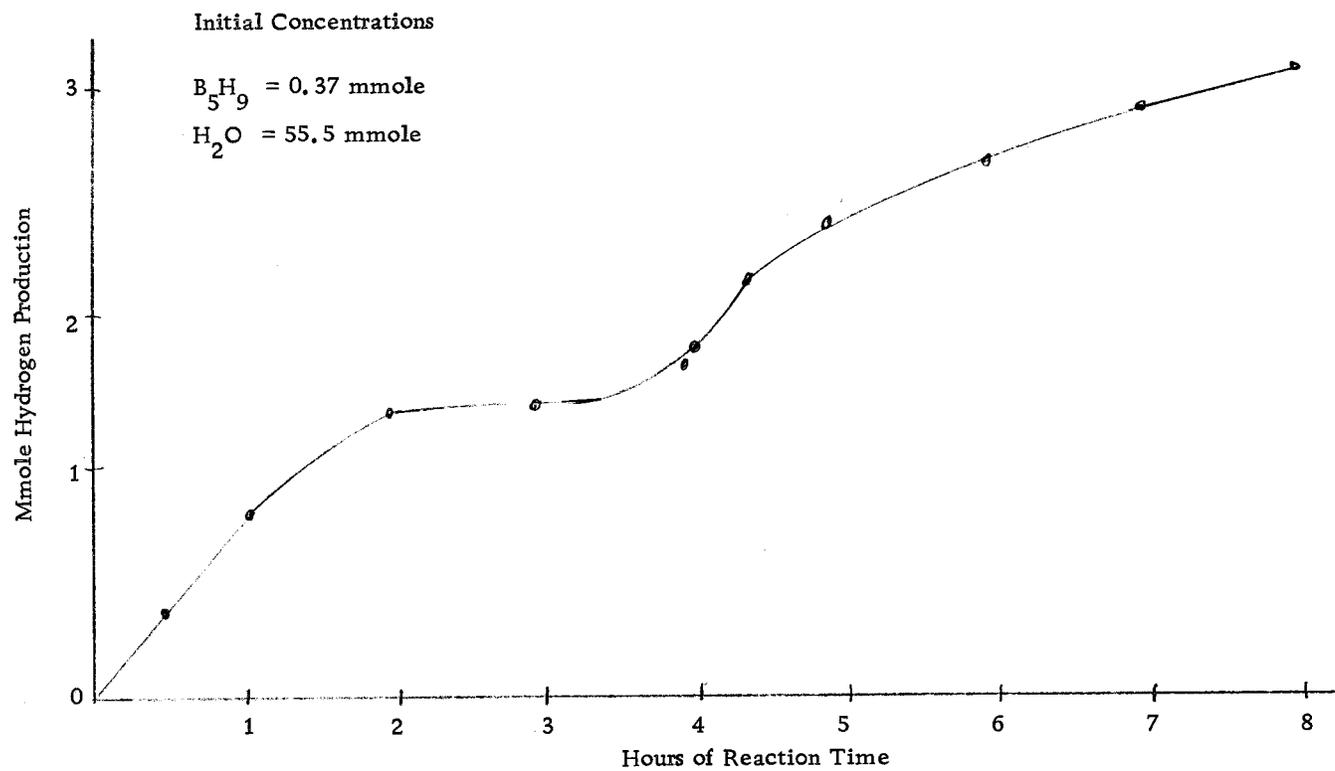
Figure 4. Production of hydrogen gas by hydrolysis of pentaborane with excess water at 150°C.

pentaborane proceeds rapidly in vivo with production of molecular hydrogen but that the hydrolysis is incomplete. Apparently a reasonably stable intermediate containing B-H bonds is formed under these circumstances. They established that the hydrolysis is catalyzed by blood and L-histidine as well as dioxane. They also observed a decrease in free amine groups in body fluids of animals injected with pentaborane. In a reaction of pentaborane with water in the presence of L-histidine they isolated a stable, solid product that gave hydrogen gas when treated with aqueous acid but it was not further characterized.

Research Objectives

The object of this research is to investigate the amine-catalyzed hydrolysis of pentaborane. In particular, intermediate hydrolysis products will be isolated, identified and characterized. The observations of Reed and co-workers indicate that reasonably stable intermediates containing B-H or B-B bonds do exist. No doubt these are stabilized by the presence of hydroxyl or nitrogen containing groups in the compounds. Hopefully, the nature of intermediates will give some information about the complex mechanism of the hydrolysis reaction of pentaborane.

EXPERIMENTAL

Apparatus and Technique

Vacuum Manipulation

All reactions and purifications of products were carried out using a conventional vacuum apparatus as described by Sanderson (86). Special apparatus were constructed when necessary and they will be described in connection with the experiment where used.

Fractional condensation was generally used for the separation of volatile mixtures. The method depends upon the fact that the residual vapor pressures of different compounds become negligible at different temperatures. Since a logarithmic relationship exists between vapor pressure and temperature, the rate of change of vapor pressure is greatest at high pressure (or temperature). A vapor pressure of .1 mm mercury or less was considered negligible.

The apparatus used in this technique is a fractionation train, Sanderson (86, p. 88-90). The fractionation is achieved by placing cold baths of decreasing temperature around U-tubes (Sanderson, 86, p. 88) in the direction of gas flow. Each component condenses in the first U-tube at which its vapor pressure is negligible so that proper selection of cold baths allows separation provided the components differ sufficiently in volatility. This method of separation

is roughly equivalent in efficiency to a distillation separation using a column of one theoretical plate. A complete description of this technique is given in Sanderson (86, p. 90). The experimental temperatures were attained using temperature baths as described by Rondeau (83).

Purity of Materials

Most generally materials were considered pure when they exhibited a vapor pressure within one percent of a value reported in the literature at the same temperature. On occasion, when the material was not volatile enough at room temperature or where the quantity of material was too small for such a measurement in a convenient volume, other methods were applied. Agreement between vapor pressures of a given sample measured in two different volumes of ratio 5:1 or greater at constant temperature was considered a criterion of purity. Under these circumstances a mixture of substances with different volatilities would show a change in vapor pressure because of the change in composition of the residual liquid phase. On other occasions a sample was split into two fractions by distilling away approximately half of the material. Coincidence of vapor pressures of the two fractions at the same temperature was indicative of purity. Finally, where critical, the purity was checked spectroscopically.

Reagents

Pentaborane

Pentaborane (B_5H_9) used in these experiments was obtained from the Callery Chemical Company, Callery Pennsylvania. The pentaborane was transferred from the stainless steel shipping cylinder to a high vacuum manifold system. The liquid pentaborane had a yellow coloration due to dissolved solid boron hydride polymers which can be detected by the eye when the concentration approaches 0.5 percent by weight (55). The pentaborane was purified to a clear liquid by distilling through a -30°C trap and condensed at -80°C. The vapor pressure was 66 mm at 0°C; the accepted value is 66 mm (98). The quantity of pentaborane used in the experiments was determined by measuring the pressure of gaseous pentaborane in calibrated volumes of the vacuum system at room temperature.

N-Octadecylamine

Technical grade n-octadecylamine (ODA), $CH_3(CH_2)_{17}NH_2$, T5787 was used as obtained from Matheson Coleman and Bell. The melting point was 48-52°C.

Hydrogen Chloride, Boron Trichloride and Trimethylamine

These compounds were obtained as technical grade compressed tank gases from the Matheson Company. Hydrogen chloride was purified by distillation through a -80°C trap and condensation at -196°C. For HCl the vapor pressure was 226 mm at -104°C; the accepted value is 226.2 mm (98). Boron trichloride was purified by distillation through a -30°C trap and condensation at -95°C. Any more volatile component was allowed to condense at -196°C. Boron trichloride was difficult to purify as it originally contained about twelve percent hydrogen chloride, which made repeated distillations necessary to establish a fair purity. For BCl_3 the vapor pressure was 479 mm at 0°C; the accepted value is 477 mm (98). Trimethylamine was purified by distillation through a -45°C trap and condensation at -196°C. For trimethylamine the vapor pressure was 79 mm at -45°C; the accepted value is 79.5 mm (2).

1, 6-Hexanediamine, n-Hexylamine and Histamine

These compounds were used as obtained. Reagent grade 1, 6-hexanediamine 5932 was obtained from Eastman Organic Chemicals. Reagent grade n-hexylamine HX400 was obtained from Matheson Coleman and Bell. Reagent grade free base histamine 12556 was obtained from K & K Laboratories and Sigma Chemical Company.

Cyclohexene

Reagent grade cyclohexene CX2355 was obtained from Matheson Coleman and Bell. The cyclohexene was purified by distillation from phosphorous pentoxide. The vapor pressure was 30 mm at 0°C; the accepted value is 30 mm (100).

Preparations and Reactions

Preparation of N-Octadecylcycloazadiboron

Water (5.0 ml) was pipetted into a reaction bulb containing 1.87 mmoles (0.50 g.) of n-octadecylamine (ODA). After evacuation and freezing at -196°C, 4.53 mmole of pentaborane was added to the reaction vessel. No reaction was evident at -80°C, -45°C and -30°C. The reaction bulb was placed in an ice bath and at 0°C the initial reaction was quite rapid as evident from an increase in pressure. At successive time intervals the reaction mixture was frozen at -196°C and the noncondensible gas removed through a -196°C trap to a calibrated volume by use of a Toepler pump. After each successive removal of noncondensible gas any material trapped at -196°C was condensed back to the reaction vessel for further reaction at 0°C. After a reaction time of 20.5 hours a total of 7.82 mmoles (Figure 5) of noncondensible gas was collected. Separation of the mixture was accomplished by warming the reaction vessel slowly to room
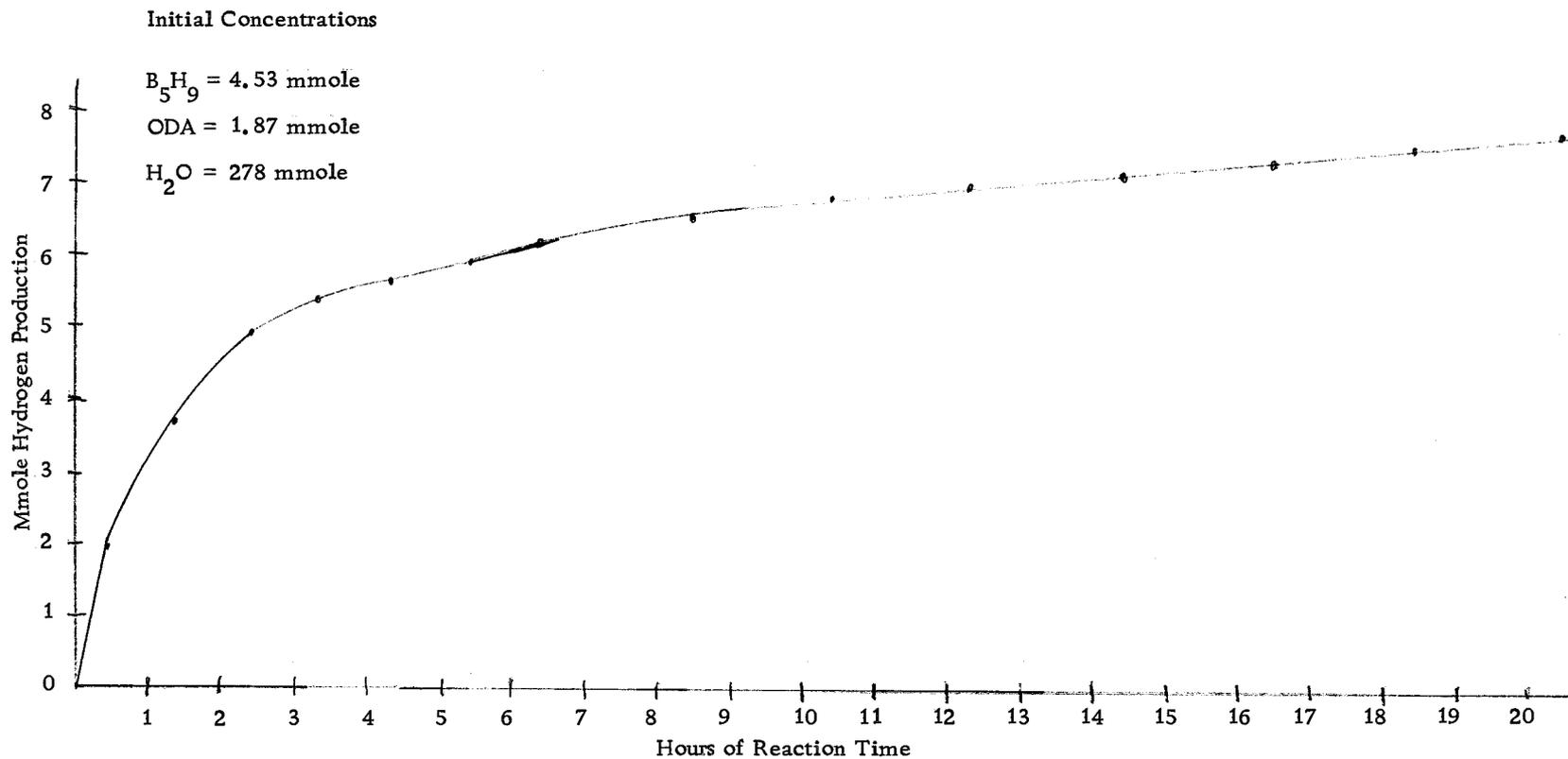
Figure 5. Production of hydrogen gas by hydrolysis of pentaborane with excess water in the presence of n-octadecylamine at 0°C.

temperature and distilling volatile material through a -30°C trap to

-196°C. Water was condensed in the -30°C trap and 0.20 mmole of

pentaborane in the -196°C trap. Nonvolatile material, after recrystal-

lization from ethanol gave 0.52 g. of a white crystalline product

m.p. 58.0-59.5°C. The white product was slightly soluble in

ethanol, methanol and chloroform. An overall yield of 95 percent

n-octadecylcycloazadiboron (CAB) was obtained based on the original

amount of ODA. One sample of CAB, crystallized from ethanol,

after 47 days at room temperature open to the air still gave hydrogen

gas in dilute acid.

By use of this method, as described above, 20 samples of CAB

were prepared. Hydrogen gas production in every preparation of CAB

was similar to that presented in Figure 5. No significant change in

the amount of hydrogen gas production was noticed by varying the con-

centration of any one of the reactants by a factor of 2X.

Physical Characterization of N-Octadecylcycloazadiboron

By use of a C & H Analyzer Model 33, Coleman Instruments

Maywood, Illinois 14.2% H and 74.8% C were found. By the Kjeldahl

method of analysis 4.1% N was found (101). A typical boron analysis

consisted of hydrolyzing a sample (0.0581) in 7 ml of 1.7 N HCl and

dilution to 250 ml with absolute ethanol. A 25.0 ml aliquot, after

titrating to the methyl red endpoint with 0.1 N NaOH and addition of

mannitol required 0.36 ml of 0.092 N NaOH (33). This and two

similar analyses of separate samples corresponds to 6.2% B. On

the basis of the elemental analysis the empirical formula $C_{18}H_{39}NB_2$

is consistent with CAB.

	% Calculated	% Found
C	74.5	74.8
B	7.3	6.2
N	4.7	4.1
H	13.5	14.2

A molecular weight of 290.1 was found for three separate

samples of the white product by use of a Vapor Pressure Osmometer

Model 301 Mechrolab Inc. Mountain View, California. Chloroform

was used as solvent and ODA as standard for the molecular weight

determination.

MW   290.6 calculated   290 $\pm$ 5 found

The infrared spectrum was determined from 650 to 4000 wave

numbers using a thin layer sodium chloride plate. A Beckman Model

IR 8 spectrophotometer was used for the determination. The infrared

spectrum of CAB is shown in Figure 6. Due to the low solubility of

CAB it was not possible to prepare a solution with a high enough

concentration to provide a H^1 or B^{11} nuclear magnetic resonance
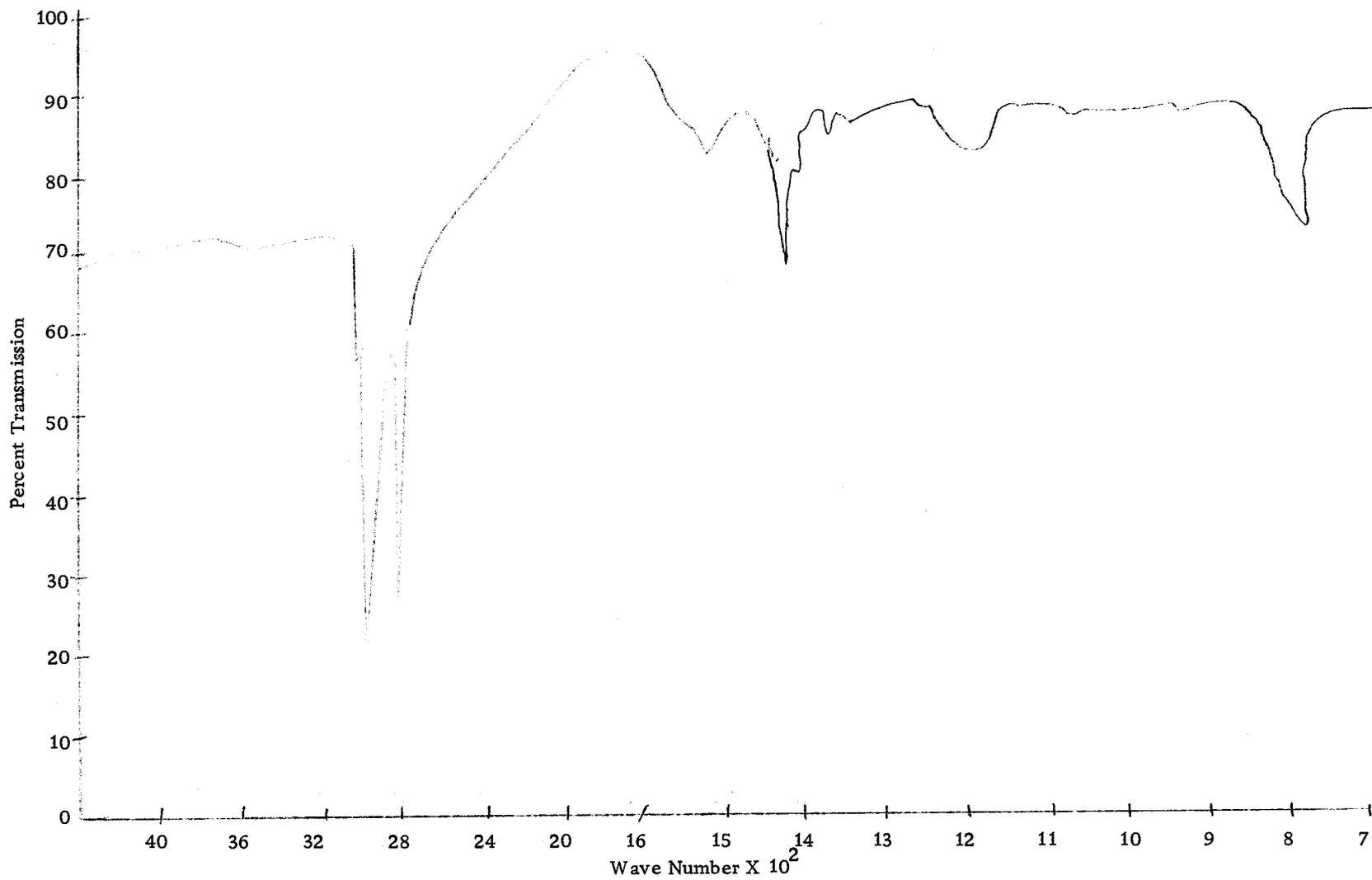
(NMR) spectrum.

Figure 6. Infrared spectrum of n-octadecylcycloazadiboron

Acid Hydrolysis of N-Octadecylcycloazadiboron

To a hydrolysis bulb was added 0.095 mmole of CAB and 5.0 ml
of 9 M sulfuric acid in separate compartments. After evacuation and
freezing at -196°C the contents of the bulb were warmed to room
temperature and allowed to come in contact. Immediate reaction was
evident by bubbling of the reaction mixture to a white foam. After 13
hours and frequent gentle heating the reaction bulb was frozen at
-196°C and 0.21 mmole noncondensible gas was recovered. The
ratio of hydrogen gas obtained to CAB used is 0.21/0.095 (H_2/CAB).
Similar results were obtained for the acid hydrolysis with five
separate samples of CAB.

Reaction of N-Octadecylcycloazadiboron with Hydrogen Chloride

Anhydrous hydrogen chloride (6.82 mmole) was added to an
evacuated reaction bulb containing 1.05 mmole CAB. The reaction
bulb was placed in a -95°C bath for 4 hours. The reaction bulb was
frozen at -196°C and 0.35 mmole noncondensible gas was recovered
by pumping through a -196°C trap. Any material present in the
-196°C trap was condensed back to the reaction bulb. The reaction
vessel was placed in a -95°C trap and HCl allowed to distill to a
-196°C trap. The recovered HCl, 4.86 mmole, passed through a
-30°C, -80°C traps and condensed at -196°C.

The recovered HCl (4.86 mmole) was condensed back into the reaction vessel in a -196°C bath. The reaction vessel was allowed to warm slowly to room temperature with the volume open to the manifold. The pressure increased slowly from the initial reading. The reaction bulb was allowed to stand for 0.5 hour at room temperature after the pressure had ceased to increase. The reaction vessel was cooled to -196°C and noncondensible gas (0.50 mmole) and HCl (5.17 mmole) were recovered. The HCl recovered had a vapor pressure of 226 mm at -104°C; the accepted value is 226.2 mm (98). A total of 1.65 mmole HCl was used in the reaction and a total of 0.85 mmole hydrogen gas was recovered for a ratio of 1.65/0.85 (HCl/H_2). Similar results were obtained by reaction of anhydrous hydrogen chloride with two separate samples of CAB.

Reaction of N-Octadecylcycloazadiboron with Boron Trichloride

Boron trichloride (6.04 mmole) was added to an evacuated reaction bulb containing 0.56 mmole CAB. The reaction bulb was placed in a 0°C ice bath for 4 hours. The reaction bulb was cooled to -196°C and 0.09 mmole of noncondensible gas was recovered by pumping through a -196°C trap. Material caught in the -196°C trap was condensed back to the reaction vessel. The reaction vessel was placed in the 0°C bath and volatile material distilled to a -196°C trap. The -196°C trap was found to contain 5.49 mmole of volatile

matter. Subsequent separation of the material in the -196°C trap provided 5.23 mmole of BCl_3 and 0.26 mmole HCl recovered. The BCl_3 passed through -30°C, -80°C and condensed at -110°C. The vapor pressure of BCl_3 at 0°C was 479 mm; the accepted value is 477 mm (98). The HCl recovered passed through -30°C, -80°C, -110°C traps and condensed at -196°C.

The reaction bulb was placed in a -196°C bath, the BCl_3 and HCl recovered were transferred back to the reaction vessel and the reaction mixture allowed to warm slowly to room temperature. No further reaction took place and after 0.5 hour, 5.23 mmole BCl_3 and 0.26 mmole HCl were recovered.

The hydrogen chloride undoubtedly was present in the initial addition of boron trichloride as difficulty in purification was cited previously. Subtracting the boron trichloride and hydrogen chloride left from the initial boron trichloride gives a total of 0.55 mmole of boron trichloride used in the reaction. The ratio of BCl_3 to CAB used is 0.55/0.56 (BCl_3/CAB). Similar results were obtained for a 2 hour reaction of CAB with BCl_3.

Reaction of Aqueous Caustic with N-Octadecylcycloazadiboron

A small amount of CAB was added to 2 N NaOH. No reaction was evident at 50-60°C for 2 hours. Similar results were obtained for the reaction of several other samples of CAB with aqueous caustic.

To a hydrolysis bulb was added 0.22 mmole (0.065 g.) of CAB and an aliquot consisting of 2.5 ml ethanol and 2.5 ml 2 N NaOH in separate compartments. After evacuation and freezing at -196°C the contents of the bulb were warmed to room temperature and allowed to come in contact. Reaction was evident by slight bubbling of the reaction mixture. The reaction bulb was heated for 0.5 hour at 50-60°C in an oil bath. After about 10 minutes at this temperature the reaction mixture became clear and the bubbling stopped. The reaction bulb was cooled to -196°C and 0.01 mmole noncondensible gas was collected. The reaction bulb was warmed slowly to room temperature. There was a white waxy material on top of the reaction mixture.

To a hydrolysis bulb was added 0.23 mmole (0.066 g.) of CAB and 5.0 ml of 9 M sulfuric acid in separate compartments. After evacuation and freezing at -196°C the contents of the bulb were warmed to room temperature and allowed to come in contact. Immediate reaction was evident by bubbling of the reaction mixture to a white foam. After 12 hours and frequent gentle heating the bubbling subsided. The reaction mixture was heated to 100°C and more reaction was noticed. All reaction subsided after heating at 80-100°C for 0.5 hour. The reaction bulb was frozen at -196°C and 0.45 mmole noncondensible gas was recovered. The ratio of hydrogen gas obtained to CAB used is 0.45/0.23 (H_2/CAB). The

reaction mixture was warmed slowly to room temperature. The

reaction bulb was opened to the air and the mixture carefully titrated

to the methyl red endpoint with 4 N NaOH. No reaction was evident

during the titration. The reaction bulb was frozen at -196°C and

evacuated with 6.0 ml of 4 N NaOH in the side compartment. The

contents of the hydrolysis bulb were warmed to room temperature

and allowed to come in contact. The reaction bulb was heated in an

oil bath at 80-100°C for 1 hour. The reaction bulb was frozen at

-196°C and 0.01 mmole of noncondensible gas was recovered. The

reaction bulb was warmed slowly to room temperature. There was

a white waxy material on top of the reaction mixture.

Reaction of N-Octadecylcycloazadiboron with Trimethylamine

Trimethylamine (6.10 mmole) was added to an evacuated bulb

containing 0.87 mmole CAB. The reaction bulb was placed in a

-45°C bath for 2 hours. The reaction bulb was cooled to -196°C

and no noncondensible gas was evident. The reaction vessel was

allowed to warm slowly to room temperature with excess tri-

methylamine distilling to a -196°C trap. A total of 6.10 mmole of

trimethylamine was recovered. The trimethylamine passed through

a -45°C trap and condensed at -196°C. The vapor pressure of

trimethylamine recovered was 77.5 mm at -45°C; the accepted value

is 79.5 mm (2). The amount of trimethylamine recovered

corresponds to the initial amount so no reaction between CAB and trimethylamine is apparent under the experimental conditions.

Cyclohexene Addition to N-Octadecylcycloazadiboron

Cyclohexene (13.24 mmole) was added to an evacuated bulb containing 0.81 mmole CAB. After two days of reaction at room temperature, the reaction bulb was placed in a 196°C bath and 0.02 mmole of noncondensible gas was removed. The reaction bulb was allowed to warm slowly to room temperature distilling the excess cyclohexene into -196°C traps. A total of 12.36 mmole of cyclohexene was recovered. A total of 0.88 mmole cyclohexene was used in the reaction. The amount of cyclohexene and CAB used in the reaction corresponds to a ratio of 0.88/0.81 (C_6H_{10}/CAB). Similar results were obtained for the addition reaction of eight other samples of CAB. CAB must be very dry for addition to cyclohexene.

Cyclohexene Reduction via N-Octadecylcycloazadiboron

By previously described methods a small amount of the addition compound was prepared using 0.97 mmole of CAB and 0.70 mmole cyclohexene. Glacial acetic acid (1.0 ml) was transferred to the addition compound in an evacuated bulb. The reaction vessel was heated for 0.5 hour at 50-60°C by an oil bath. The reaction mixture was observed to bubble initially but this subsided after about ten

minutes. The reaction bulb was placed in a -196°C bath and 0.80 mmole noncondensible gas was removed. The reaction bulb was allowed to warm to room temperature and volatile products were distilled through a -30°C trap to -196°C. Acetic acid was found in the -30°C trap. The material in the -196°C trap was distilled through a-95°C trap and condensed at -196°C several times. Cyclohexane 0.30 mmole was isolated in the -95°C trap as subsequently determined by a vapor pressure of 27 mm at 0°C; the accepted value is 27 mm at 0°C (100). Cyclohexene 0.01 mmole was isolated in the -196°C trap as subsequently determined by a vapor pressure of 30 mm at 0°C; the accepted value is 30 mm at 0°C (100). A gaseous infrared spectrum study of the products differentiated cyclohexene by the =CH stretching peak at 3020 wave numbers $(\bar{v})$, the CH out of plane deformation peak at 690 $\bar{v}$ and C=C at 1660 $\bar{v}$ from cyclohexene. This method provides a small yield, 43%, of cyclohexane based on the original amount of cyclohexene used. The amount of hydrogen gas obtained from the reduction process and CAB used corresponds to a ratio of 0.80/0.97 (H_2/CAB). Similar results were obtained for the reduction reaction with two other samples of CAB.

Off Gas from N-Octadecylcycloazadiboron

A small amount of CAB was prepared in the usual manner starting with 1.88 mmole ODA, 5.0 ml water and 5.02 mmole

pentaborane. After a reaction time of 9 hours a total of 7.00 mmole noncondensible gas was collected. The product was separated in the usual manner by removing all volatile material. Pentaborane (0.12 mmole) was collected. The product was kept under vacuum at room temperature. At various time intervals the reaction bulb was placed in a -196°C bath and noncondensible gas removed. During 35 days a total of 0.65 mmole of noncondensible gas was collected from the reaction product. The reaction product was crystallized from methanol and dried in a vacuum desiccator over calcium chloride. The product bubbled in dilute hydrochloric acid.

Reaction of Aqueous N-Hexylamine with Pentaborane

Water (5.0 ml) was pipetted into a reaction bulb containing 3.79 mmole n-hexylamine. After evacuation and freezing at -196°C, 2.14 mmole pentaborane was added to the reaction bulb. The reaction bulb was placed in an ice bath and at 0°C slight reaction was evident by increasing manometer readings. After a reaction time of 1.5 hour, 1.60 mmole of noncondensible gas was collected. Separation was accomplished by warming the reaction vessel slowly to room temperature and distilling through a -30°C trap to -196°C. No solid product was evident.

Reaction of Aqueous 1, 6-Hexanediamine with Pentaborane

Water (5. 0 ml) was pipetted into a reaction bulb containing 10. 3 mmole 1, 6-hexanediamine. After evacuation and freezing at -196°C, 2. 05 mmole pentaborane was added to the reaction bulb. The reaction bulb was placed in an ice bath and at 0°C slight reaction was evident by increasing manometer readings. After a reaction time of 1 hour, 1. 33 mmole of noncondensible gas was collected. Separation was accomplished by warming the reaction vessel slowly to room temperature and distilling through a -30°C trap to -196°C. No solid product was evident.

Reaction of Aqueous Histamine with Pentaborane

Water (5. 0 ml) was pipetted into a reaction bulb containing 4. 6 mmoles (5. 1 g.) histamine. After evacuation and freezing at -196°C, 4. 13 mmole pentaborane was added to the reaction bulb. The reaction bulb was placed in an ice bath and at 0°C slight reaction was evident by increasing manometer readings. At successive time intervals the reaction was frozen at -196°C and noncondensible gas removed. After each successive reading, the reaction vessel was placed in an ice bath for further reaction at 0°C. After a reaction time of 12 hours a total of 7. 49 mmoles of noncondensible gas (Figure 7) was collected. Separation was accomplished by warming the

Figure 7. Production of hydrogen gas by hydrolysis of pentaborane with excess water in the presence of histamine at 0°C.

reaction bulb slowly to room temperature and distilling through a

-30°C trap to -196°C. Water was found in the -30°C trap and 1.98

mmole pentaborane in the -196°C. The pentaborane vapor pressure

was 66 mm at 0°C; the accepted value is 66 mm (98). Histamine

(4.8 mmole, 5.3 g.) was recovered by recrystallization from hot

methanol. However, the histamine recovered did not bubble in dilute

hydrochloric acid indicating absence of any B-H bonding. Similar

results were obtained by use of two pure histamine samples from

different vendors and hydrogen gas production was similar to that

presented in Figure 7.

Reaction of Aqueous Impure Histamine with Pentaborane

Water (10.0 ml) was pipetted into a reaction bulb containing

4.49 mmole (0.50 g.) histamine, $C_5N_3H_9$, (Sigma Chemical Company

Lot No. 114B-5110). After evacuation and freezing at -196°C, 4.45

mmole pentaborane was added to the reaction bulb. No reaction was

evident at -80°C, -45°C and -30°C. The reaction bulb was placed

in an ice bath and at 0°C the initial reaction was quite rapid as

evident from an increase in pressure. At successive time intervals

the reaction mixture was frozen at -196°C and the noncondensible

gas removed through a -196°C trap. After each successive removal

of noncondensible gas any material trapped at -196°C was condensed

back to the reaction vessel for further reaction at 0°C. After a

reaction time of 14 hours a total of 8.45 mmole of noncondensible

gas (Figure 8) was collected. Separation of the reaction mixture was

accomplished by warming the reaction bulb slowly to room tempera-

ture and distilling volatile material through a -30°C trap to -196°C.

Water was condensed in the -30°C trap and 1.24 mmole pentaborane

in the -196°C trap. The pentaborane vapor pressure was 66 mm at

0°C; the accepted value is 66 mm (98). Nonvolatile material, after

recrystallization from methanol, gave 0.078 g. of a white crystalline

product m.p. 117.5-118.9°C. The white product was slightly

soluble in ethanol, methanol and chloroform. The white product,

open to the air, gave hydrogen gas in dilute acid.

By use of this method, as described above, 19 samples of the

white product were prepared. Hydrogen gas production in every

preparation was similar to that presented in Figure 8. No significant

change in the amount of hydrogen gas production was noticed by

varying the concentration of any one of the reactants by a factor of

2X.

By use of a C & H Analyzer, previously described, 68.1% C

and 14.3% H was found. By the Kjeldahl method of analysis 4.6% N

was found (101). A typical boron analysis consisted of hydrolyzing

a sample (0.0272 g.) in 7 ml of 1.7 N HCl and dilution to 250 ml
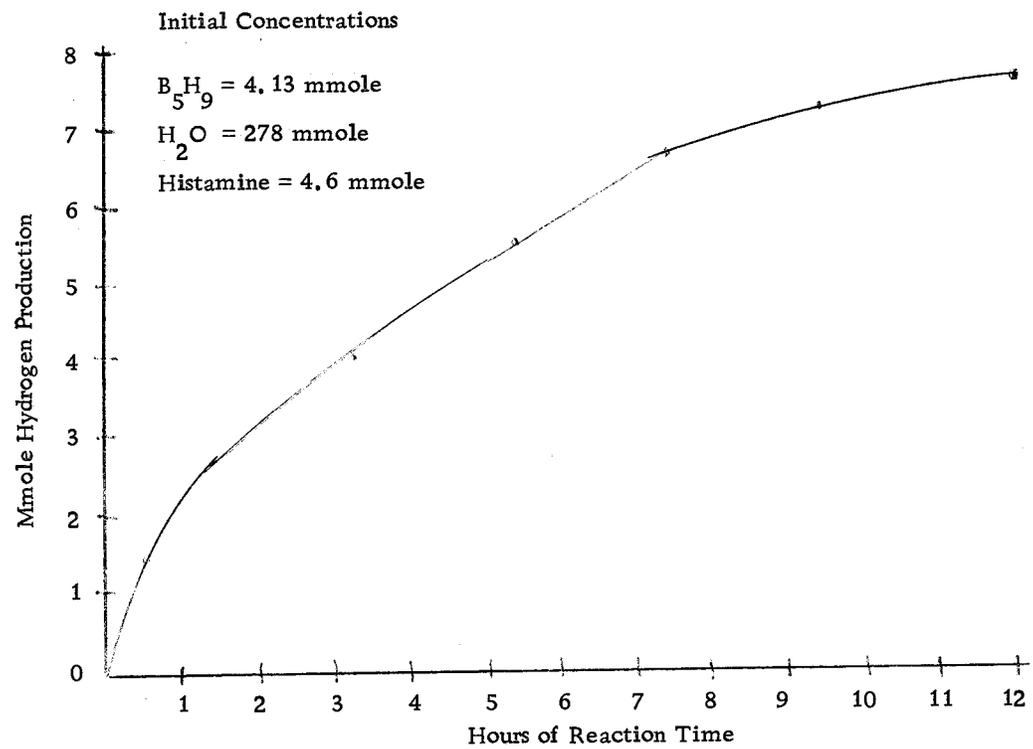
with absolute ethanol. A 25.0 ml aliquot, after titrating to the methyl
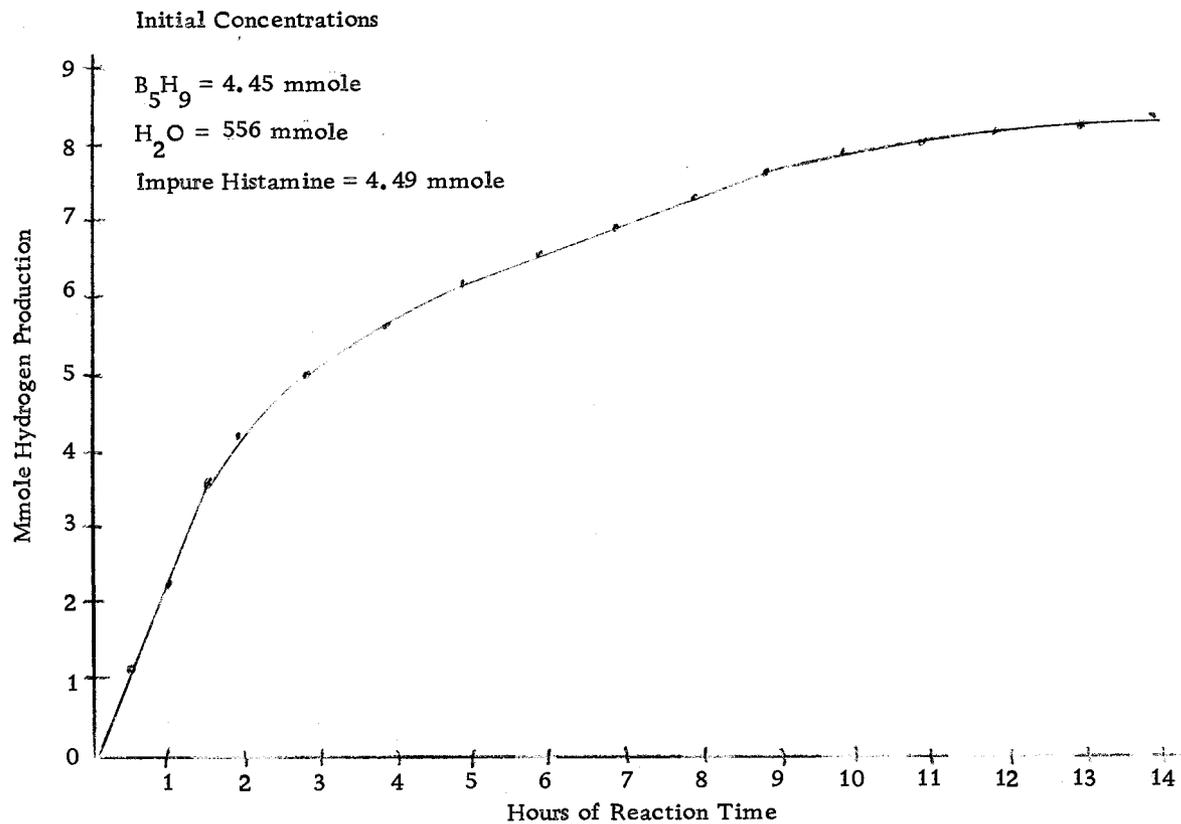
Figure 8.   Production of hydrogen gas by hydrolysis of pentaborane with excess water in the presence of impure histamine at 0°C.

red endpoint with 0.1 N NaOH and addition of mannitol required

0.165 ml of 0.123 N NaOH (33). This and three similar analyses of

separate samples corresponds to 8.0% B. Similar analyses were

obtained from two referees and agreed in all cases. The empirical

formula $C_{17}NH_{43}B_2$ is calculated on the basis of the elemental

analysis.

	% Calculated	% Found
C	72.1	68.1
H	15.3	14.3
N	4.9	4.6
B	7.9	8.0

Acid hydrolysis of a 0.016 g. sample of the white product,

by previously described methods, produced 0.33 mmole of non-

condensible gas. The white product (0.0631 g.) was reacted with

anhydrous hydrogen chloride, by previously described methods, for

6 hours at -95°C. A total of 3.10 mmole HCl was used and 3.30

mmole of noncondensible gas was collected.

DISCUSSION OF RESULTS

The hydrolysis of pentaborane-9 was shown to be catalyzed by long chain amines, specifically octadecylamine (ODA), but not by short chain amines or diamines. Thus, n-hexylamine and 1,6-hexanediamine did not catalyze the hydrolysis reaction appreciably, the rate of hydrogen gas production being only slightly higher than the uncatalyzed reaction. The catalysis of the reaction by histamine reported by Reed and co-workers (82) was shown to be catalysis by a major impurity in the histamine leading to a product containing carbon and nitrogen in the ratio of 17 to 1. Degradation of the histamine structure,

$$HC - N - CH_2 - NH_2$$
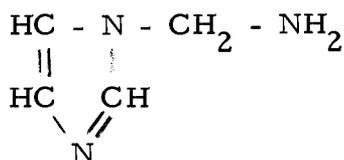
appears very unlikely to give any residue approaching this carbon-nitrogen ratio. Furthermore, it was found that authentic histamine does catalyze the hydrolysis reaction somewhat, but does not give a solid intermediate resembling the product reported by Reed (82)

Catalysis by a long chain amine but not short chain amines may be accounted for as primarily a surface effect. Hydrolysis takes place at the pentaborane-water interface and the presence of

an amine coordinated to pentaborane (presumably at a basal boron) may well make the boron cage more subject to attack by water. Lack of catalysis by short chain amines may result from different orientation of the complexes at the surface, or simply a concentration effect arising from the much greater solubility in water of the short chain amines.

Butler and co-workers (18) reported an acceleration in rate of the gas phase hydrolysis after the initial reaction (Figure 4). This increase in rate was not observed in this reaction, perhaps because of stabilization of the intermediate by coordination with amine, or an entirely different mechanism for the amine-catalyzed reaction.

The intermediate hydrolysis product isolated contains two boron atoms per octadecylamine group. Although both nitrogen and boron analyzed slightly low, a known characteristic of compounds in which these atoms are bonded to each other, the B-N ratio analyzed at 1.96 B: 1.00 N. The yield of product was 95% based on octadecylamine. The product from many preparations melted reproducibly at 58.0-59.5°C. The greatest question about the structure of the NB_2 portion of the compound arises in connection with the number of hydrogens bonded to the nitrogen and boron atoms, and their bonding arrangement. Because of the large number of hydrogens (37) in the octadecyl group, total hydrogen analysis does not reveal this information. The experimental molecular weight of 290 and the

elemental analysis indicate a formula, $C_{18}H_{37}NB_2H_x$, but other experimental evidence must be used to determine the value of x.

Six structures are considered possible on the basis of the analysis and molecular weight:
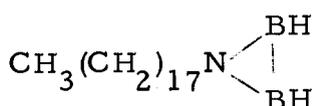
$$CH_3(CH_2)_{17}N\begin{matrix} BH \\ | \\ BH \end{matrix}$$

I

Calc. Mol. Wt. = 290.6

$$CH_3(CH_2)_{17}\overset{+}{N}\begin{matrix} H & BH_2^- \\ | \\ BH \end{matrix}$$

II

Calc. Mol. Wt. = 292.6

$$CH_3(CH_2)_{17}\overset{H\ H}{N=B}-BH_2$$

III

Calc. Mol. Wt. = 292.6

$$CH_3(CH_2)_{17}\overset{H\ H}{N-B}\overset{H}{\underset{H}{\diagdown}}BH_2$$

IV

Calc. Mol. Wt. = 294.6

$$CH_3(CH_2)_{17}N\begin{matrix} H & BH_2 \\ & \diagdown \\ & BH_2 \end{matrix}H$$

V

Calc. Mol. Wt. = 294.6

$$[CH_3(CH_2)_{17}NH]\,BH_3^+\,BH_4^-$$
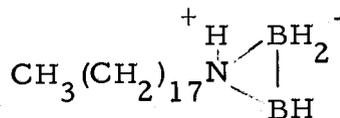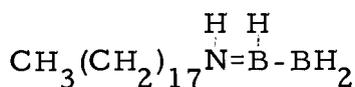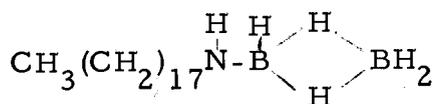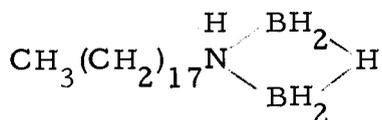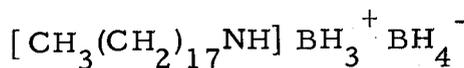
VI

Calc. Mol. Wt. = 296.6

All six structures give molecular weights well within experimental error if it is presumed that VI is undissociated in chloroform solution. Only V has a structure analagous to a known compound, B_2H_7N, in which the octadecyl group is replaced by a hydrogen. The predominant weight of chemical evidence indicates structure I,

named n-octadecylcycloazadiboron (CAB), as the most probable struc-

ture.

The aqueous acid hydrolysis of the compound CAB yields two

moles of hydrogen gas per mole of compound. This is the expected

result for CAB:

$$CH_3(CH_2)_{17}N\underset{BH}{\overset{BH}{<}} \overset{|}{} + 2H_2O \overset{H^+}{\longrightarrow} CH_3(CH_2)_{17}N\underset{BOH}{\overset{BOH}{<}} \overset{|}{} + 2H_2$$
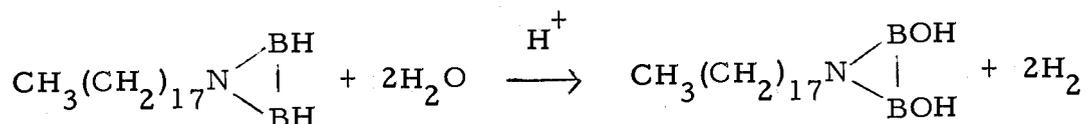
Compounds II, III, IV and V would be expected to give three, three,

five and five moles of hydrogen gas, respectively, per mole of com-

pound. Compound VI might give four or seven moles of hydrogen gas

per mole of compound depending upon whether the cation is stable in

aqueous acid solution:

$$[CH_3(CH_2)_{17}NH] BH_3^+BH_4^- + 3H_2O + H^+ \longrightarrow [CH_3(CH_2)_{17}NH_3]BH_3^+ + 4H_2 + H_3BO_3$$
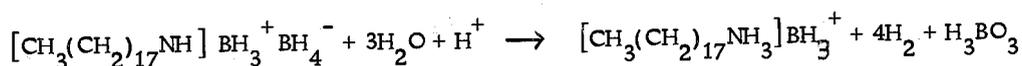
There is no evidence to support the stability of the ion in aqueous

acid solution, in fact, the analagous diammomiate of diborane is

known to hydrolyze completely under these conditions (90).

$$[(NH_3)_2BH_2]^+BH_4^- + 6H_2O + 2H^+ \longrightarrow 2NH_4^+ + 2H_3BO_3 + 6H_2$$
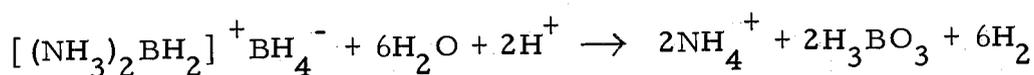
Thus, compound I (CAB) appears to be the only possibility that can

yield so small an amount of hydrogen gas upon acid hydrolysis.

A three-membered ring of the cycloazadiboron type has not been

observed before in boron derivatives. An analagous structure may
be present in known amine and ammonia addition compounds of boron
cages such as the hydrides or carboranes but have not been deter-
mined. The ring is resonace-stabilized by pi-bonding:

$$R \; N \overset{BH}{\underset{BH}{\big|}} \quad \longleftrightarrow \quad R\text{-}N \overset{BH}{\underset{BH}{\big|}}$$

Alternatively, this can be described, using molecular orbital
terminology as a three-center pi bond.

The nature of the products of reaction of CAB with anhydrous

HCl and BCl_3 are not known but may be inferred by analogy with

observations of Wiberg (102) on reactions of amino boranes. Wiberg (102)

determined that $CH_3HNB(CH_3)_2$ absorbs an equivalent amount of HCl

at room temperature:

$$\begin{matrix} CH_3 & & CH_3 \\ & N\text{-}B & \\ H & & CH_3 \end{matrix} + HCl \longrightarrow \begin{matrix} CH_3 & & Cl \\ & N\text{-}B & \\ H_2 & & (CH_3)_2 \end{matrix}$$
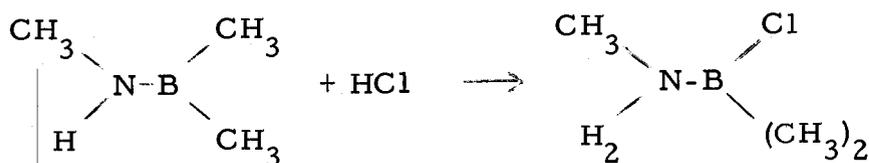
The analagous reaction of CAB yields $\quad CH_3(CH_2)_{17}N \overset{H \quad BH}{\underset{BH \\ Cl}{\big|}}$

However, in this compound one boron has a vacant P_z orbital, no

longer stabilized by dative bond formation with nitrogen. Further

reaction with HCl would be expected, with the product stabilized by

back-coordination from chlorine to boron:

$$CH_3(CH_2)_{17}N\underset{\overset{|}{\underset{Cl}{BH}}}{\overset{H}{\overset{|}{BH}}} + HCl \longrightarrow CH_3(CH_2)_{17}N\underset{\overset{|}{B=Cl:}}{\overset{H}{\overset{H}{\underset{|}{BCl}}}} + H_2$$
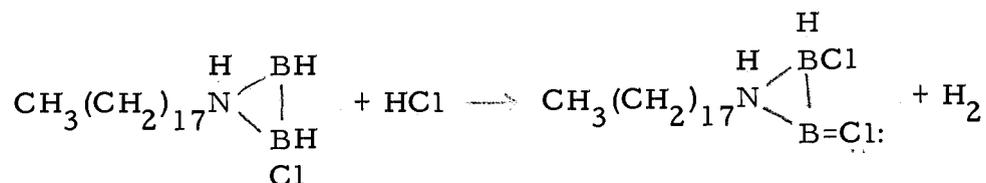
The stoichiometry of these reactions, one mole CAB absorbing two moles of HCl and giving one mole of hydrogen gas, is in accordance with experimental observations. It should be noted that Compounds IV, V and VI would all give diborane as a product of the reaction with anhydrous HCl.

CAB was observed to absorb one mole of BCl_3 per mole and to be unreactive toward trimethylamine at -45°C. The BCl_3 addition product is obvious:

$$CH_3(CH_2)_{17}N\underset{\overset{\backslash}{BH}}{\overset{\overset{\overset{BCl_3}{|}}{-}\,BH}{}}$$
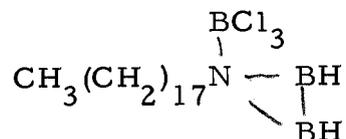
Unreactivity toward trimethylamine can only be attributed to the resonance stabilization of the ring.

Cyclohexene was established to add 1:1 to CAB at room temperature. No evidence was determined for the 2:1 compound. The addition of 2 moles of cyclohexene to 1 mole of CAB should be theoretically possible. However, steric hindrance may be a major factor favoring the 1:1 addition compound due to the comparatively large size of the cyclohexene ring and the very long side chain. The

addition of cyclohexene to CAB followed by hydrolysis with acetic

acid produces cyclohexane in 43% yield. It is significant that one

mole of hydrogen gas per mole of CAB was produced in the hydrolysis

reaction. This establishes the reaction with cyclohexene as a

hydroboration rather than B-B addition to the C=C double bond.

$$CH_3(CH_2)_{17}N\diagup\diagdown \begin{matrix} BH \\ | \\ BH \end{matrix} + C_6H_{10} \longrightarrow CH_3(CH_2)_{17}N\diagup\diagdown \begin{matrix} BC_6H_{11} \\ | \\ BH \end{matrix}$$

$$CH_3(CH_2)_{17}N\diagup\diagdown \begin{matrix} BC_6H_{11} \\ \\ BH \end{matrix} + 2H_2O \xrightarrow[50-60°C]{HOAC} CH_3(CH_2)_{17}N\diagup\diagdown \begin{matrix} BOH \\ | \\ BOH \end{matrix} + C_6H_{12} + H_2$$
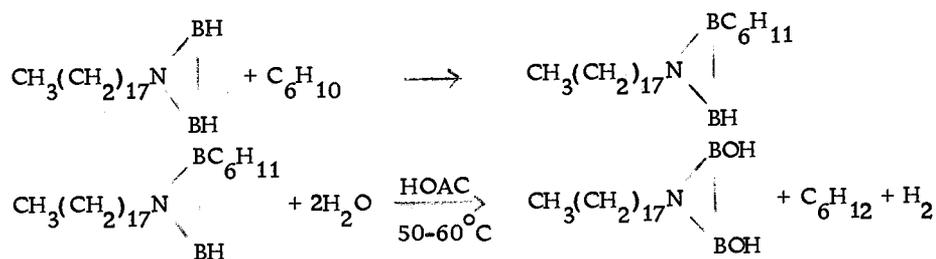
If the reaction were B-B addition to the double bond, two moles of

hydrogen gas per mole of CAB·C_6H_{10} would be expected on hydrolysis.

The unreactivity of CAB toward aqueous base is noteworthy.

Hydrogen bonded to tetravalent boron is known to be quite stable

toward basic hydrolysis. For example, the borohydride ion, BH_4^-,

is stable in basic aqueous solution in the absence of polarizing cations.

However, compounds containing this ion yield diborane in aqueous

acid (90). It is not unreasonable that the resonance stabilization of

the three-membered ring in CAB protects it from nucleophilic attack

by OH^- just as with $(CH_3)_3N$.

Compound II, a dative-bonded three-membered ring structure,

may be the precursor to CAB. It was noted throughout this work that

the initial solid product from the hydrolysis reaction had to be stored

in a dessicator for several days before further use even though it appeared to be dry in less than one day. If it were used before three days for further reaction nonstoichiometric, unreproducible results were obtained. One sample, stored in a vacuum line immediately after separation from the hydrolysis mixture, was observed to produce small amounts of hydrogen gas for about one week. This suggests a slow dehydrogenation which may be

$$CH_3(CH_2)_{17}N \overset{H}{\underset{BH}{\overset{BH_2}{|}}} \longrightarrow CH_3(CH_2)_{17}N \overset{BH}{\underset{BH}{\overset{|}{|}}} + H_2$$
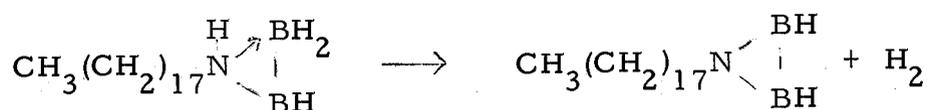
The mechanism of the hydrolysis reaction of pentaborane is obviously not established by this work. However, there are several conclusions which may be drawn from this work. The suggestion of Butler and co-workers (18) that all terminal hydrogens hydrolyze before the boron cage structure or bridging hydrogens are attacked can not apply in the case of the amine-catalyzed reaction. The absence of -OH groups on the borons of CAB preclude such a mechanism. It appears most likely that one of the two borons in CAB is the apical boron in the pentaborane structure. Basal borons in pentaborane are bonded by B-H-B bridge bonds. Only the apical boron is bonded to other borons by two-center bonds. The creation of a B-B bond from a bridge bond is unlikely under the conditions of this reaction.

The hydrolysis mechanism might be elucidated by a mass spectrum study of the reaction products by using apical substituted deuteriopentaborane or B^{10} enriched pentaborane. The position of the labeled (D or B^{10}) atom in the CAB structure would provide valuable mechanism information.

A nuclear magnetic resonance (NMR) B^{11} spectrum by a time averaging transients could distinguish whether the borons in CAB are equivalent or not. Equivalent borons in CAB would be an indication of three-center pi bonding.

An x-ray diffraction study is needed to establish the structure of CAB. If the first carbon attached to the NB_2 ring is found to be planar to the NB_2 ring this would indicate three-center pi bonding.

Research is needed to synthesize and characterize compounds similar to CAB, but with small side chains. Such a compound may be prepared by reacting aqueous pentaborane with a large excess of methylamine for a long time. A study is needed of the hydrolysis of the addition compound between ammonia and pemtaborane, which may provide a compound similar to CAB with no side chain.

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