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Synthesis and properties of substituted borazoles

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SYNTHESIS AND PROPERTIES OF SUBSTITUTED BORAZOLES

by

Gerd Helmut Dahl

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INTRODUCTION

Borazole, $B_3N_3H_6$, possesses a six-membered ring structure of alternate boron and nitrogen atoms. Its physical constants

$$\begin{array}{c}
H \\
| \\
B \\
H-N \quad\quad N-H \\
| \quad\quad\quad | \\
H-B \quad\quad B-H \\
N \\
| \\
H
\end{array}$$
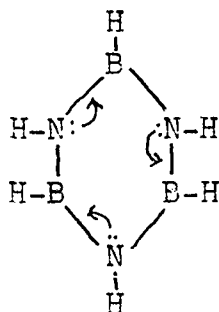
are remarkably similar to those of benzene with which it is isosteric and isoelectronic. The older literature abounds in comparisons of borazole compounds with their respective benzene analogs; yet, the dissimilarity of the atoms in the molecule and the polarity of the bonds results in a behavior which is peculiar only to borazoles. The existence of a free pair of electrons on the nitrogen atoms are responsible for a certain degree of aromaticity of the ring which is clearly expressed in the reduced bond distances between the boron and the nitrogen atoms as compared to the boron nitrogen distance in trimethylamine borane. This double bond character in turn places a negative and a positive formal charge on the boron and the nitrogen atoms, respectively. In contrast to benzene where all hydrogen atoms are equivalent there are two possible sites on the borazole ring for chemical reactions, one on the boron atoms and one on the nitrogen atoms.

With these structural peculiarities of the borazole ring in mind, it was intended in the following work to explore further the chemical reactions of the borazole nucleus. These studies were performed on borazole and its halogen derivative, B-trichloroborazole, $B_3Cl_3N_3H_3$.

REVIEW OF LITERATURE

Borazole, of which there are now known numerous derivatives, was first prepared by Stock and Pohland in 1926 (52). While examining the reaction between ammonia and various boron-hydrides, these first investigators discovered that diborane or tetraborane and ammonia react at $200^{\circ}C$ to form a liquid compound of the empirical composition BNH_2. Vapor density measurements indicated the molecular formula $B_3N_3H_6$. On the basis of its thermal stability, Stock and Pohland believed that the compound contained alternate boron and nitrogen bonds. Thus, they suggested as the most probable structure a six-membered ring composed of three equivalent boron and three equivalent nitrogen atoms.

Striking chemical evidence was collected by Stock and his students to support the symmetrical "benzene" type structure. Thus, borazole was found to add water or hydrogen chloride in a 1:3 molar ratio (53).

Similarly, a methyl derivative of borazole, B-trimethyl-N-trimethylborazole was found to yield upon hydrolysis equimolar quantities of only methyl boric acid and monomethylamine (62). This could only be explained by the presence of equivalent boron and nitrogen atoms in the borazole molecule.

Finally, Schlesinger and his co-workers undertook an exhaustive study of the various possible methyl derivatives of borazole (45, 46). The number of isomers of methyl

derivatives found could only be justified by the assumption
of a six-membered ring structure of borazole.

Structural investigations further confirmed the six-
membered ring configuration of borazole. It was shown by
electron diffraction that the borazole molecule possesses D_{3h}
symmetry which corresponds to the D_{6h} symmetry of the benzene
molecule (3, 54). According to these studies, borazole was
found to have a planar arrangement of atoms with a bond angle
of 120° and a boron nitrogen distance of 1.44 $\overset{O}{A}$. This bond
distance lies between those observed for single (1.54 $\overset{O}{A}$) and
double (1.36 $\overset{O}{A}$) boron nitrogen bonds and suggests a partial
double bond character which was estimated to be 28% (50).

The Raman spectrum of borazole showed all the active
vibration frequencies which one would expect by analogy of
its structure to that of benzene (14). The ultraviolet
spectrum of borazole determined in the range of 4600 $\overset{O}{A}$ to
1700 $\overset{O}{A}$ revealed two absorption bands analogous to bands found
for benzene at higher wavelengths. A third band appearing
in benzene was found to be missing in the borazole spectrum
but believed to be hidden between the other two bands (27,
36). The infrared spectrum of borazole was first investigated
in 1939 (14), and a more detailed assignment of the absorp-
tion bands was made by Price et al. in 1950 (37). Mass
spectrometric studies of borazole and its chloro and methyl
derivatives have been made most recently (32). It was found

that the borazole ion loses a hydrogen atom more readily
than the benzene ion. By comparison of the appearance poten-
tials of the $B_3N_3H_5^+$ and the $C_6H_5^+$ ion, the authors suggested
that probably a B-H bond rather than an N-H bond is broken
to give the $B_3N_3H_5^+$ ion.

An approximate molecular orbital treatment of borazole
has been attempted from the ultraviolet spectrum using a
semiempirical approach which had also been applied to the
benzene molecule (38). Considering the difference in elec-
tronegativity for the boron and the nitrogen atoms in borazole
as an additional parameter, the treatment gave a value of
-2.3 e.v. for the bond integral between boron and nitrogen.
This agreed well with the value of -2.6 e.v. determined for
the benzene molecule.

Subsequent to Stock's original preparation a number of
attempts have been made to improve upon the laboratory prep-
aration of borazole. Schlesinger and co-workers prepared
borazole in 30-35% yields from ammonium chloride and lithium
borohydride at high temperatures (42). More recently Russian
workers have reported an improved yield of 40% by this method
(33). Similarly, Emeleus and Videla obtained borazole by
heating a mixture of hydrazine hydrochloride and lithium
borohydride (18).

Other preparations of borazole reported involved the
reduction of compounds in which the borazole skeleton was

already present. Thus, B-trichloroborazole was reduced by
lithium borohydride or sodium borohydride in various solvents
(24, 44). These reactions, however, require special experi-
mental techniques to handle the toxic and explosive diborane
which is liberated in the reduction. Recently, Hohnstedt
and Leifield described the reduction of B-trichloroborazole
with triisopropoxy hydroborate in isopropylborate as solvent
which avoids the liberation of diborane; however, only a max-
imum yield of 20% could be realized by this method (23).
Attempts to repeat these experiments in this laboratory were
unsuccessful.

Inorganic and organic derivatives of borazole can be
obtained by two methods. One procedure involves reactions
in which the borazole nucleus is synthesized during the re-
action; the second method utilizes reactions of suitable re-
agents with compounds that already possess a borazole nucleus.

B-trichloroborazole and B-tribromoborazole have been
prepared by the interaction of ammonium chloride or hydrazine
hydrochloride and boron trichloride or ammonium bromide or
hydrazine hydrobromide and boron tribromide (9, 10, 17). An
older method, but less satisfactory for synthetic purposes
involves the thermal decomposition of the 1:3 adduct of
borazole with hydrogen chloride or hydrogen bromide (61).

The partially halogenated borazoles, B-monochlorobora-
zole, B-dichloroborazole, and the corresponding bromo com-

pounds have been isolated from the reaction of borazole with boron trichloride and boron tribromide (42). Borazole undergoes addition reactions with hydrogen chloride, hydrogen bromide, water and alcohols (60). The products have been assumed to be cyclohexane type derivatives, although no confirmation of this has yet been obtained.

The preparation of a B-trifluoroborazole has been unsuccessfully attempted by the reaction of B-trichloroborazole with hydrogen fluoride (25).

Attempts to prepare derivatives by direct substitution of the halogen in B-trichloroborazole with inorganic salts in suitable solvents have also been made. The reactions between silver cyanide, silver nitrate and trichloroborazole in acetonitrile were investigated, but the products which still contained chlorine could not be identified (9).

The preparation of B-halogenated borazoles in which an organic group is attached to the nitrogen atoms has been given considerable attention since these compounds serve as convenient intermediates for the synthesis of other organic borazoles. B-trichloro-N-trimethylborazole has been prepared from methylamine hydrochloride and boron trichloride (22, 56). B-trifluoro-N-trimethylborazole was isolated from the reactions of monomethylamine with dimethylboron fluoride (64). Jones and Kinney reported a reaction between aniline and boron trichloride from which they obtained B-trichloro-N-triphenyl-

borazole (29).

These halogenated borazoles have been used for substitution reactions to prepare B-alkylated compounds. Thus, B-trichloro-N-triphenylborazole was allowed to react with various Grignard reagents to obtain B-trialkyl-N-triphenyl-borazoles (20). Similar reactions were run with B-trichloro-N-trimethylborazole and Grignard reagents (39). B-trialkoxy-and B-triphenoxy-borazoles were obtained from the treatment of B-trichloro-N-trimethylborazole with sodium alkoxide and sodium phenoxide (8). A convenient preparation of various N-substituted borazoles has been accomplished by the reduction of the corresponding chloro compounds with sodium borohydride in various polyethylene glycol dimethyl ethers (22).

Other borazoles have also been used to prepare organic derivatives. Trichloroborazole was found to react with diazomethane to form B-tris-(monochloromethyl)borazole, $B_3(CH_2Cl)_3N_3H_3$ (55). B-trichloro-N-phenylborazole upon treatment with alkyl or aryl lithium or suitable Grignard reagents formed the corresponding B-substituted borazoles (49). Trichloroborazole itself was methylated to B-trimethyl-borazole by reacting it with a methyl Grignard in ether solution (47).

Various organo borazoles have also been synthesized by procedures similar to the one used to prepare the parent compound employing ammonia derivatives and suitable boron com-

pounds. B-methylated borazoles were first synthesized by Schlesinger et al. from methyldiborane and ammonia (45); a more convenient preparation from ammonia and boron trimethyl was reported later by Wiberg et al. (63). N-methylated borazoles have been prepared by reacting diborane with methylamine (46, 63) or by heating methylamine hydrochloride with lithium borohydride (41). Wiberg and Hertwig reported the synthesis of hexamethylborazole from trimethyl boron and monomethylamine (62). B-tributyl, B-triphenyl, and B-trivinylborazole were obtained from the reaction of ammonia with the corresponding monosubstituted boron trichloride (7).

In a patent Gould first described the synthesis of B-aminoborazoles from B-trichloroborazole and excess amine (19). Recently, Niedenzu and Dawson prepared a B-aminoborazole, B-tris(diethylamino) borazole with ethylamine hydrochloride or by allowing ammonia to react with dichloro-(diethylamine)-borane, $BCl_2N(C_2H_5)_2$ (35). By using monoethylamine in place of ammonia the authors were also able to prepare B-tris(diethylamine)-N-triethylborazole by the latter method.

Earlier work on the preparation of organo borazoles and their properties has been adequately reviewed elsewhere (4, 58, 59, 60).

EXPERIMENTAL

Apparatus and Materials

Borazole compounds except for the highly substituted organic derivatives are frequently somewhat moisture sensitive and have to be carefully protected from contact with air. This was best accomplished by handling these compounds in a high vacuum system. The preparations and purification of reagents were also performed under high vacuum conditions unless otherwise stated. The construction and operation of high vacuum systems need not be discussed here; it has been adequately reviewed elsewhere (40, 51).

In isotope exchange reactions and the preparation of isotopically substituted borazoles care was exercised to exclude contamination from atmospheric water by flaming out the entire glass system of the high vacuum line and by using sealed reaction vessels whenever possible.

A Perkin Elmer Infracord Spectrophotometer Model 137 was used to obtain infrared spectra. For infrared spectra of gaseous materials, a gas cell of 100 cc. volume with sodium chloride windows was employed. Mass spectra were obtained with a Consolidated Engineering Mass Spectrometer, Model 21-620. Only mass peaks above $m/e = 74$ were reocrded to idantify and detect isotopic exchange on borazole. The samples were run at pressures of 75-100μ using an ionizing

current of 20 milliamperes.

Since acetonitrile is an excellent solvent for some in-organic salts, it was frequently used in substitution reactions. However, in order to avoid decomposition reactions, it was found necessary to carefully purify the acetonitrile. The most satisfactory purification method was found to be one recommended by Wawzoneck and Runner (57). This required the treatment of acetonitrile with saturated potassium hydroxide solution, drying over anhydrous sodium carbonate and phosphoric anhydride, and the subsequent distillation from phosphoric anhydride in a good fractionating column.

Diethylene glycol dimethyl ether which was occasionally used as a solvent was freed from moisture by refluxing over calcium hydride. The dried product was then distilled from lithium aluminum hydride, and a fraction boiling at 160°-$164^{\circ}C$ was collected. The ether was obtained from the Ansul Chemical Company under the trade name Ansul 141.

Ethylene glycol dimethyl ether, which was also used as a solvent was obtained from the Ansul Chemical Company and was freed from moisture by refluxing over sodium.

For the reaction of chloral with borazole, the anhydrous reagent was prepared by distilling chloral hydrate from sulfuric acid.

Pyridine which was used in the formation of an adduct with trichloroborazole was stored over calcium hydride and

then distilled on a small Podbielniak column. The fraction

coming over at 115°C was collected. Ortho-xylene which was

employed as a solvent in the same reaction was redistilled

and a fraction boiling at 143-144°C was retained.

Samples of monophenylsilane and diphenylsilane which were

available in this laboratory were used without further purifi-

cation. Azomethane which served as a source of free radicals

was prepared from dimethylhydrazine hydrochloride (28). The

latter was synthesized by a procedure described by Hatt (21).

The crude azomethane was purified by vacuum distillations

through a -80°C bath and a -112°C bath, and pure azomethane

was collected in the -112°C bath. Another free radical ini-

tiator, α,α'-azodiisobutyronitrile was obtained from the

Eastman Kodak Chemical Company.

The tri-n-butylamine used in the reduction of trichloro-

borazole was of practical grade obtained from the Eastman

Kodak Chemical Company. It was freed from impurities of

primary and secondary amines by distillation from acetic

anhydride.

The B-trichloroborazole used for metathetic substitution

reactions was prepared earlier in this laboratory from boron

trichloride and ammonium chloride (9). The crude product was

further purified by sublimation in a vacuum.

For the reaction with trichloroborazole potassium thio-

cyanate was dehydrated by heating it in air to its melting

point. Silver cyanide which was commercially available was dried in vacuum prior to its use. Reagent grade silver nitrate, also used in substitution reactions with B-trichloroborazole, was used without further purification.

Borazole was initially prepared by the reduction of B-trichloroborazole with sodium borohydride in diethylene glycol dimethyl ether in an atmosphere of helium. The crude product was freed from ether and diborane by repeated fractional distillations in a high vacuum system. The ether was trapped in a -45°C bath while the more volatile borazole was retained in a -95°C bath which permitted the diborane to pass through. The pure borazole had a vapor pressure of 85 mm which agreed with the value reported in the literature (61). Borazole was later prepared by a simplified procedure which will be described in a subsequent section.

The deuterium oxide as well as deuterium gas used for exchange reactions was obtained commercially from the Liquid Carbonic Company, San Carlos, California, and the Stuart Oxygen Company, San Francisco, California, and were claimed to be of greater than 99.5% purity.

The preparation of reagents for isotopic exchange reactions with borazole was performed as follows. Deuterated ammonia was prepared from magnesium nitride and deuterium oxide and purified by high vacuum distillations through a -95°C bath which retained less volatile impurities. The

magnesium nitride had been prepared by heating magnesium turnings in a stream of dry nitrogen at 800°C in mullite tubing. Analysis of the deuterium content of the ammonia was achieved by decomposing a sample on a red hot platinum wire and measuring the hydrogen-deuterium ratio mass spectrometrically (30). Ammonia samples of better than 96% purity in deuterium were obtained.

Calcium phosphide used for the synthesis of phosphine was prepared by a thermite reaction from calcium orthophosphate in the presence of aluminum (?). Deuterated phosphine was then generated by the treatment of the calcium phosphide with deuterium oxide. It was purified by distillation through a -112°C bath, which retained the less volatile impurities. The purified deuterated phosphine had a vapor pressure of 171 mm at -112°C as compared to the reported value of 170 mm at -112°C for phosphine (16).

Deuterium chloride was synthesized by reacting silicon tetrachloride with deuterium oxide (2). The final product which had been purified by repeated distillations through a -112°C bath had a vapor pressure of 119 mm at -112°C as compared to 120 at -112°C reported for hydrogen chloride (16).

Deuterium cyanide was formed by the hydrolysis of potassium cyanide with deuterium oxide in the presence of phosphoric anhydride. The potassium cyanide had been previously dried by heating in vacuum. The deuterium cyanide was dis-

tilled repeatedly through a $-65.5^{\circ}C$ bath into a $-95^{\circ}C$ bath.
Only the fraction in the $-95^{\circ}C$ bath was retained which had a
vapor pressure of 263.5 mm at $0^{\circ}C$ as compared to the reported
value of 265 mm at $0^{\circ}C$ for hydrogen cyanide (16).

Deuterium sulfide was prepared in vacuum from dried fer-
rous sulfide and deuterium oxide in the presence of phos-
phoric anhydride, and purified by repeated distillations
through a $-112^{\circ}C$ bath which retained less volatile impurities.
The vapor pressure of deuterium sulfide was 16.5 mm at $-112^{\circ}C$
as compared to 16 mm reported for hydrogen sulfide (16).

Deuterated ethanol in which the hydrogen in the hydroxyl-
group was substituted by deuterium was available in the de-
partment from Dr. Shiner's research group, Indiana University.
Upon analysis by the combustion and density measurement of
the resulting hydrogen deuterium mixture, the ethanol was
shown by Dr. Shiner's group to be 98% deuterated in the
hydroxyl-group.

Deuterated acetylene was prepared in vacuum from calcium
carbide and deuterium oxide. The vapor pressure of the
deuterated acetylene which was purified by repeated distilla-
tions through a $-112^{\circ}C$ bath was found to be 66 mm at $-112^{\circ}C$
as compared to the literature value of 67 mm for acetylene at
$-112^{\circ}C$ (16).

Samples of 91% deuterated diborane were available in the
laboratory and had been prepared several years ago in Professor

Schlesinger's research group, University of Chicago. The
deuterium content of the deuterated diborane was determined
by Mr. Gerald Brennan in this laboratory. A sample of the
diborane was reduced over iron at 1000°C and the amount of
deuterium in the resulting hydrogen-deuterium mixture was
determined mass spectrometrically. The vapor pressure of
the purified deuterated diborane was 238 mm at -112°C.

Deuterated sodium borohydride was prepared by heating
sodium borohydride in the presence of deuterium (13). Before
exchange the sodium borohydride was purified by a procedure
outlined by H. C. Brown et al. (12). An infrared spectrum of
a sample of the deuterated borohydride which was dissolved in
diglyme showed on the basis of the relative intensity of the
B-H and the B-D absorption bands that more than 50% deutera-
tion had taken place.

Decaborane used to investigate the reaction with borazole
was available in the laboratory and was purified by sublima-
tion in the vacuum system. The study of the reaction of
borazole with acetic acid was performed with 99.8% pure glacial
acetic acid from the Baker Chemical Company.

Reactions of B-Trichloroborazole

Reaction of B-trichloroborazole
with potassium thiocyanate

B-trithiocyanatoborazole was prepared by allowing B-tri-
chloroborazole to react with potassium thiocyanate. In a

typical reaction 4 g. of B-trichloroborazole and 6.5 g. of
potassium thiocyanate, corresponding to a mole ratio of 1:3,
were dissolved in separate 75 cc. portions of solvent and
filtered in vacuum from any undissolved residues. The
B-trichloroborazole solution was slowly added to the ether
solution of potassium thiocyanate, carefully excluding the
presence of air. Immediate precipitation of potassium chlor-
ide resulted accompanied by the evolution of heat. The solu-
tion was then filtered under dry nitrogen, and the solvent was
removed by vacuum distillation. The remaining solid was re-
crystallized from fresh solvent and finally washed with dry
hexane.

Acetonitrile was also tried as a solvent but was found to
be unsatisfactory since occasionally the thiocyanate solution
decomposed leading to gummy, highly colored reaction products.

The purified thiocyanatoborazole was obtained in about
60% yield as a white faintly yellow, at room temperature non-
sublimable powder which melted with decomposition in vacuum
at 147-150°C. Like trichloroborazole this compound reacted
rapidly with water to form ammonia, boric acid, and thiocyanic
acid. Upon exposure to the atmosphere trithiocyanatoborazole
turned yellow.

For analysis the compound was hydrolyzed in aqueous
solution. The thiocyanate ion content was determined gravi-
metrically as silver thiocyanate, and the boric acid was

titrated in the presence of mannitol. The ring nitrogen was
obtained by the Kjeldahl method. The following analytical
results were obtained for trithiocyanatoborazole: Analysis:
Calculated for $B_3(SCN)_3N_3H_3$: B, 12.8; SCN^-, 69.2; N(ring),
16.7. Found: B, 12.6; SCN^-, 68.4; N(ring), 16.6. The
molecular weight was determined by the cryoscopic method in
benzene: Calculated, 253; Found, 251.7.

Reaction of B-trichloroborazole with silver cyanide

B-tricyanoborazole was prepared by allowing B-trichloro-
borazole to react with a suspension of silver cyanide in
acetonitrile. A quantity of 22 g., 0.164 mole, of silver
cyanide was placed in a round bottom flask of 100 cc. volume
with several grams of glass beads. A solution of 7 g., 0.038
mole of B-trichloroborazole in about 60 cc. of acetonitrile
was then added in the presence of an atmosphere of dry nitro-
gen. The reaction flask was attached to a shaker and agitated
for one week to assure that the substitution was complete.
During this time the reaction was carefully protected from
light to prevent the photochemical decomposition of the silver
chloride formed. The contents of the flask were then fil-
tered from silver chloride and the excess silver cyanide, and
the precipitate was extracted several times with fresh por-
tions of acetonitrile. The filtrate and washings were com-
bined, and the solvent was removed in vacuum. The remaining

white precipitate was recrystallized six times from aceto-
nitrile.

The compound was white when pure, and unlike trichloro-
borazole it was thermally stable in vacuum to temperatures
exceeding 200°C. B-tricyanoborazole was found to be insolu-
ble in benzene, toluene, carbon tetrachloride and hexane but
was soluble in acetonitrile at room temperature to the extent
of 0.6-0.7 g. in 100 cc. of solvent.

The cyanoborazole was sensitive toward moist air, and in
water it immediately hydrolyzed to liberate hydrogen cyanide.
Attempted reduction with lithium borohydride and sodium
borohydride led to the formation of tar-like unidentifiable
products.

In spite of several recrystallizations the purest reac-
tion product contained nearly 5% silver by weight, possibly
as a silver cyanide complex. For the determination of the
ring nitrogen by the Kjeldahl method, the cyanide present was
precipitated with a slight excess of silver nitrate. The
solution was then filtered into a Kjeldahl flask and digested.
Boron was determined in the usual manner by titration in the
presence of mannitol. The cyanide ion content was determined
by a titration with silver nitrate by the Liebig method, and
the silver impurities were titrated with potassium thiocya-
nate. Analysis of B-tricyanoborazole gave the following re-
sults: Calculated for $B_3(CN)_3N_3H_3$: B, 20.8; N(ring), 27.0;

CN⁻, 50.2; Found: B, 18.4; N(ring), 24.6; CN⁻, 45.2; Ag,
4.8. If these analytical results are recalculated the mole
ratio of boron to ring nitrogen to cyanide to silver is found
to be 1.00:1.03:1.02:0.03.

Reaction of B-trichloroborazole with silver nitrate

Quantities of 3.48 g., 18 mmoles, of trichloroborazole
and 9.6 g., 56 mmoles, of silver nitrate were dissolved in
separate portions of 30 cc. of acetonitrile. Since it was
found in preliminary experiments that the reaction products
decomposed above 0°C, the solutions were cooled to -18°C. The
silver nitrate solution was added to the borazole solution in
an atmosphere of dry nitrogen, and immediate precipitation
of silver chloride occurred. After standing overnight in a
deep freeze chamber the reaction mixture was filtered while
the low temperature was maintained, and the excess solvent
was pumped from the filtrate at -10°C. Crystals began to
form, which melted upon slight warming, and more acetonitrile
could be pumped off. The solvent could not be completely re-
moved at these low temperatures. Upon standing at room
temperature for 15 hours, the white syrupy residue had turned
yellow and had given off large quantities of nitrogen dioxide.
The residue ignited with a brilliant green flash in the gas
flame and decomposed instantaneously on a hot plate to form
nitrogen dioxide and a white refractory material.

The stoichiometry of the reaction of silver nitrate with B-trichloroborazole was crudely tested by adding 15.5 mmoles of trichloroborazole to 52.6 mmoles of silver nitrate at $-10^{o}C$. The filtrate from this reaction was found to contain silver ions but no chloride ions. It appeared that all three chloride ions had been replaced in the B-trichloroborazole molecule.

The reaction product obtained below $0^{o}C$ was extracted with anhydrous diethyl ether, and a solid material which retained ether and was insoluble in hexane was recovered from the extract. The solid material appeared to undergo little decomposition to nitrogen dioxide at room temperature over a period of a week, and only a slight color change from white to light yellow had occurred. The reaction of water with this material was explosively violent accompanied by ignition.

In another experiment the reaction product obtained in acetonitrile was treated with dry toluene at $-5^{o}C$. Whereas it appeared to be insoluble at this temperature, some reaction took place as was indicated by the formation of bubbles and a color change from white to yellow. The toluene could not be completely removed again by vacuum distillation and a syrupy pink residue remained. The latter was extracted with portions of ether. Upon distillation of the ether at $-8^{o}C$ a whitish pink solid came out of solution, and before the distillation was completed, the residue in the flask exploded

most violently.

Unsuccessful substitution reactions
of B-trichloroborazole

Other substitution reactions of B-trichloroborazole were
attempted with potassium cyanate in acetonitrile; with lithium
bromide in acetonitrile and in 1,2 dimethoxyethane; with
mercuric iodide in methyl iodide; with the etherate of mag-
nesium perchlorate in acetonitrile; and with aluminum bromide
in toluene. In no case was a reaction observed.

A reaction, however, took place in acetonitrile with
thallium cyclopentadiene in which thallous chloride precip-
itated out, but the supernatant liquid quickly decolorized
and a definite product could not be isolated. For the same
reason, the reaction of B-trichloroborazole in cyclopentadiene
was unsuccessfully investigated.

Reaction of B-trichloroborazole
with anhydrous chloral

Amounts of 1.4 g. of B-trichloroborazole and 6.7 g. of
anhydrous chloral were introduced into a flask of 25 cc.
volume which was then sealed off. All the trichloroborazole
was in solution at room temperature. Upon heating for 15
minutes on the steam bath, a white precipitate was formed.
The flask was opened, and traces of hydrogen chloride were
observed; however, no chloroform could be isolated which would

be one expected reaction product had a formylation reaction
taken place (6). Upon distillation in vacuum, a syrupy
material remained which still contained an easily hydrolyzed
chlorine compound.

Reaction of B-trichloroborazole with pyridine

To a solution of 0.376 g., 2.04 mmoles, of trichloro-
borazole dissolved in 3.530 g. of o-xylene were added 1.083
g., 13.68 mmoles of pyridine. Immediate formation of a white
precipitate occurred, and when the reaction was completed the
solvent and excess pyridine were removed by distillation in
vacuum. Subtracting the weight of the solvent, it was found
that 0.55 g., 7.07 mmoles, of pyridine were recovered. Thus,
apparently 6.61 mmoles of pyridine had reacted with 2.04
mmoles of trichloroborazole to form a product containing tri-
chloroborazole and pyridine in a 1:3.24 molar ratio. The
solid reaction product which melted with decomposition in
vacuum at 145-150°C was insoluble in organic solvents, but
was found to be soluble with reaction in water.

Analysis were performed on the crude product from the
reaction of trichloroborazole with pyridine. Boron was
determined by the titration of boric acid in the presence of
mannitol. The chlorine present was determined volumetrically
by the Mohr method, and the total nitrogen content was ob-
tained by the Dumas method through the services of the micro-

analyst in the Department of Chemistry, Indiana University.
Analysis gave the following results: Calculated for
$B_3N_3H_3Cl_3 \cdot 3$pyridine: B, 7.7; N, total, 20.0; Cl, 25.5;
Found: B,8.4; N, total, 19.9; Cl, 28.8.

Reaction of B-monochloroborazole with hydrogen chloride

Monochloroborazole was prepared by reacting boron chloride with borazole at room temperature (42). The desired product was isolated from the side-products and excess borazole by fractional distillation in the vacuum system.

Into a reaction flask of 50 cc. volume equipped with a magnetic breaker, were sealed 0.076 mmole of monochloro-borazole, $B_3ClH_2N_3H_3$, and 0.350 mmole of hydrogen chloride. Upon standing for 28 hours at room temperature, a white, non-volatile precipitate had formed in the flask, and 0.122 mmole of unreacted hydrogen chloride was recovered. Thus, 0.076 mmole of monochloroborazole had reacted with 0.228 mmole of hydrogen chloride to form a 1:3 adduct.

Thermal stability of the hydrogen chloride adduct of monochloroborazole   A quantity of 0.103 mmole of the hydrogen chloride adduct of monochloroborazole was heated at $95^{\circ}C$ for one hour, and 0.003 mmole of hydrogen was liberated. Upon heating for another hour at $127^{\circ}C$, an additional 0.003 mmole of hydrogen was liberated. When heated for two additional hours at $150^{\circ}C$, 0.002 more mmole of hydrogen was

evolved, and essentially all of the solid in the flask had disappeared. Volatile materials were collected in a liquid nitrogen cold bath. Upon warming to room temperature some of the volatile material appeared to react to form a solid. The rest was lost during a transfer in the vacuum system.

Reduction of B-trichloroborazole

Reactions of B-trichloroborazole with monophenylsilane and diphenylsilane   Small quantities of B-trichloroborazole and diphenylsilane were introduced into a flask of 50 cc. volume. Traces of iodine were added, and the reaction mixture was irradiated with ultraviolet light for 30 minutes. Since no material more volatile than diphenylsilane was found in the reaction flask, a reduction to borazole had not occurred. Similarly, no reduction was observed to have taken place when B-trichloroborazole and diphenylsilane were irradiated with ultraviolet light in the presence of azomethane.

In another experiment, α, α'-azodiisobutyronitrile, also a free radical initiator, was added to solution of trichloroborazole in monophenylsilane. The reaction mixture was briefly heated to $80^\circ C$. Upon fractionation in the high vacuum system, only nitrogen, some silane, trichloroborazole and monophenylsilane were recovered.

Samples of trichloroborazole were heated with diphenyl-silane, as well as monophenylsilane at $70^\circ C$ for 1° hours.

Small amounts of non-condensable gas, presumably hydrogen, were detected, but no reduction products of trichloroborazole could be isolated. Upon heating to 180°C for 40 hours, a definite reaction appeared to have taken place between tri-chloroborazole and diphenylsilane. The nature of this re-action was not investigated further after it had been estab-lished by infrared spectra that none of the reaction products contained boron-nitrogen bonds.

In another reaction monophenylsilane was added at room temperature to an o-xylene solution of trichloroborazole and aluminum chloride. Large amounts of silane, which was iden-tified by its vapor pressure, were isolated, but the presence of compounds containing boron-nitrogen bonds was not observed. This same reaction was repeated unsuccessfully with α, α'-azodiiso butyronitrile present as a free radical initiator. The reaction mixture was heated briefly to 60°C and then for 95 minutes at 80°C.

Reaction of B-trichloroborazole with sodium hydride in the presence of sodium borohydride Amounts of 24.3 g. of trichloroborazole, 26 g. sodium hydride, and 2 g. sodium borohydride were introduced into a 500 cc. flask containing glass beads and 75 cc. of diglyme. The container was attached to a shaker and agitated for three days. Large amounts of hydrogen had formed, but no borazole could be isolated from the volatile materials in the flask.

Reaction of B-trichloroborazole and sodium borohydride in the presence of triethylamine   About 5 g. of sodium boro-hydride were dissolved in 50 cc. of diglyme; to this solution were added 8 g. of triethylamine. The reaction flask which was equipped with a side arm was attached to the vacuum system, and a solution of 4.8 g. of trichloroborazole in diglyme was carefully introduced by means of a separatory funnel. The mixture was stirred vigorously for two hours. A material readily volatile in vacuum was removed and freed from ether by passing through a -45°C cold bath. An infrared spectrum taken in a gas cell revealed the presence of nitrogen-hydrogen bonds and boron-hydrogen bonds in this material, and a mass spectrum showed the compound to be bora-zole, though considerably contaminated with triethylamine. Due to the similar volatility, a satisfactory way of separat-ing borazole from triethylamine in the high vacuum system was not found.

Reaction of B-trichloroborazole with sodium borohydride in the presence of tri-n-butylamine   Several preliminary investigations of the reduction of trichloroborazole with sodium borohydride in the presence of tri-n-butylamine were made to assure that the reduction proceeded smoothly without liberation of the highly toxic and explosive diborane. A typical reduction on a larger scale was performed in a 2-liter, three-necked flask equipped with a mechanical

stirrer; the flask was charged with 77 g. of sodium boro-
hydride dissolved in 600 cc. of diglyme. With vigorous
stirring 380 g., a 25% excess, of tri-n-butylamine were added
to the flask which had been chilled to 0°C. The reaction
flask was flushed with a slow stream of nitrogen, and a solu-
tion of 100 g. of trichloroborazole in 250 cc. of diglyme was
added to the flask dropwise over a period of one hour. The
stirring was continued for 30 minutes after the addition was
complete.

The reaction flask was attached to a spiral reflux con-
denser, cooled with a salt-ice bath, and the reaction mixture
distilled in high vacuum, first at room temperature and later
with gentle heating to 40-50°C. Borazole and some ether col-
lected in a dry ice cooled trap. The crude borazole was
transferred to a Podbielniak distillation column which had
been previously flushed with dry nitrogen. The "cold finger"
in the distilling head was cooled with circulating brine and
the mixture was distilled at atmospheric pressure. The receiv-
ing flask was cooled with an ice bath and a fraction of 20 g.
(corresponding to an approximate 46% yield) boiling at 54.5°C
were collected. The vapor pressure of this fraction was 86
mm at 0°C compared to 85.3 mm for pure borazole. A gas
chromatogram showed one additional component to be present to
the extent of less than one per cent. Mass spectrometric
investigation of the impurity which was separated by conven-

ticnal vacuum techniques failed to identify the component but
showed it to be boron free. Infrared examination showed the
substance to contain carbon-hydrogen bonds. The material
apparently arose from ether cleavage.

Reactions of Borazole

Isotope exchange reactions of borazole

**Reaction of borazole with deuterated ammonia and
N-deuterated diethylamine**   In a flask of 3 cc. volume, 0.73
mmole of deuterated ammonia was mixed with 0.23 mmole of
borazole, and the mixture was allowed to remain at $-50^{\circ}C$ for
about five minutes. Upon fractionation through a $-95^{\circ}C$ bath
which retained borazole it was found that 0.56 mmole of
ammonia and 0.12 mmole of borazole could be recovered. The
highest peak in the mass spectrum of the recovered borazole
had a value of $m/e = 84$ as compared to $m/e = 81$ for borazole
of ordinary isotopic composition indicating that exchange had
taken place with only three hydrogen atoms in the borazole
molecule. Infrared spectra showed that partial exchange had
taken place on the nitrogen atoms. The characteristic N-H
bands at 2.8μ and 13.9μ for borazole had decreased in in-
tensity and a N-D band at 3.8μ, partially superimposed on
the B-H band, appeared.

To investigate a possible reaction in the gas phase be-
tween borazole and deuterated ammonia, 0.13 mmole of borazole

was mixed with 0.48 mmole of deuterated ammonia at room temperature. This was done in a reaction vessel which consisted of two bulbs of 50 cc. volume each and which was sufficiently large to accommodate the reactants in the gas phase. The two glass vessels were connected by a 4 mm high vacuum stopcock. The reactants were condensed into the bulbs, and after warming to room temperature the ammonia was expanded into the bulb containing the borazole by opening the stopcock. After standing for 25 minutes, the deposition of small amounts of a white precipitate was observed. A mass spectrum on the recovered borazole showed that no exchange had taken place.

The exchange reaction at low temperatures with N-deuterated diethylamine was performed by a method similar to that described for ammonia. An amount of 0.12 mmole of borazole was allowed to react with 0.41 mmole of N-deuterated diethylamine for three minutes at -30°C. Since the separation of the reagents proved difficult, a mass spectrum of the recovered mixture was taken. It revealed that three hydrogens in the borazole molecule had undergone exchange.

Reaction of borazole with deuterated phosphine   Exchange reactions were attempted under various experimental conditions. In a reaction vessel of 5 cc. volume 0.14 mmole of borazole was allowed to remain at -49°C with 0.65 mmole of deuterated phosphine for five minutes. Similarly, 0.11 mmole of borazole and 0.62 mmole of deuterated phosphine were

allowed to remain at room temperature for 26 hours. A quan-
tity of 0.15 mmole of borazole was heated with 0.72 mmole of
deuterated phosphine in the gas phase at $135^{\circ}C$ for one hour.
Finally, 0.13 mmole of borazole and 0.60 mmole of deuterated
phosphine were allowed to remain at $-80^{\circ}C$ for two hours. A
liquid phase of phosphine was evident at this temperature.
In all cases it was impossible to induce an exchange or a
chemical reaction between borazole and deuterated phosphine,
and a practically quantitative recovery of the reactants could
be achieved.

Reaction of borazole with deuterium chloride   Amounts
of 0.14 mmole of borazole and 0.63 mmole of deuterium chloride
were condensed into a 5 cc. reaction flask and allowed to
warm to room temperature. Formation of a solid occurred and
upon standing for 15 minutes the remaining reactants were
separated by fractional distillation through a $-95^{\circ}C$ bath
which retained only borazole. The mass spectrum of the re-
covered borazole showed peaks only up to $m/e = 84$ indicating
that only three hydrogen atoms of the borazole molecule had
undergone exchange. An infrared spectrum of the recovered
borazole indicated by disappearance of the N-H band that just
as in the reaction with ammonia the hydrogen on the nitrogen
atoms was involved in the exchange.

In another experiment 0.64 mmole of deuterium chloride
and 0.17 mmole of borazole were mixed in the gaseous phase at

room temperature in a reaction flask described earlier for
the gas phase reaction between deuterated ammonia and bora-
zole. The reaction mixture was allowed to stand for 10 min-
utes. During this time a non-volatile white precipitate
formed on the walls of the reaction vessel. Upon fraction-
ation of the volatile contents, 0.25 mmole of deuterium
chloride and 0.03 mmole of borazole were recovered. There-
fore, 0.39 mmole of deuterium chloride had reacted with 0.14
mmole of borazole. This result is in fair agreement with
earlier observations that the reaction between borazole and
hydrogen chloride lead to the formation of a 1:3 adduct (53).
Again it could be shown by a mass spectrum of the recovered
borazole that exchange between borazole and deuterium chloride
had taken place.

Reactions of the deuterium chloride adduct of

borazole   About 0.02 mmole of borazole was allowed to stand
in the gas phase at room temperature over 0.19 mmole of the
deuterium chloride adduct of borazole which was deposited on
the walls of a reaction flask of 50 cc. volume. After three
hours all of the borazole was recovered, and a mass spectrum
showed that no measurable hydrogen-deuterium exchange had
taken place between the solid adduct and the gaseous borazole.

In a flask of 100 cc. volume 0.18 mmole of the deuterium
chloride adduct of borazole was heated with 1.49 mmoles of
triethylamine at 85°C for seven hours. The reaction mixture

which contained 0.04 mmole of a non-condensable gas, presumably hydrogen, was distilled through a -95°C bath which retained 0.05 mmole of borazole that had undergone isotopic exchange. Mass peaks up to m/e = 84 were observed in the mass spectrum of the recovered borazole; however, the site of isotopic substitution was not established since a sufficient amount of sample was not available.

Thermal stability of the hydrogen chloride adduct of borazole   A quantity of 0.102 mmole of the hydrogen chloride adduct of borazole was heated at 100°C for one hour, and 0.007 mmole of hydrogen was formed which was pumped off. Upon heating to 110°C for one hour, 0.010 mmole of hydrogen had been liberated. When heated for two more hours at 130°C, a total of 0.015 mmole of hydrogen had been formed. By increasing the temperature to 138°C and heating for two hours the total yield of hydrogen was increased to 0.032 mmole. Finally, after additional heating at 155°C for two and one half hours an overall amount of 0.05 mmole of hydrogen had been liberated. Small amounts of condensable gas, presumably hydrogen chloride, had also been formed, and some non-volatile solids remained in the reaction flask.

Reaction of borazole with deuterium cyanide and hydrogen cyanide   Amounts of 0.51 mmole of borazole and 2.07 mmole of deuterium cyanide were mixed in the gas phase at room temperature for one hour. During this time no visible reac-

tion had occurred, and no isotope exchange had taken place as shown by a mass spectrum on the gas mixture. However, when the reaction flask was briefly chilled to obtain a liquid phase, a white precipitate formed immediately. Some unreacted borazole was still present after the flask had warmed to room temperature again. Its mass spectrum revealed that a partial exchange of hydrogen by deuterium had taken place.

To examine the stoichiometry of the reaction between borazole and hydrogen cyanide, a reaction between 3.85 mmoles of hydrogen cyanide and 0.52 mmole of borazole was allowed to go to completion by repeated cooling until no more white precipitate was formed. An amount of 2.20 mmoles of hydrogen cyanide was recovered; thus, the overall reaction, as in the case of the hydrogen chloride adduct of borazole, corresponded to a 1:3 adduct represented by the formula, $B_3N_3H_6 \cdot 3HCN$.

Properties of the hydrogen cyanide adduct of

borazole   The hydrogen cyanide adduct was soluble in diglyme, insoluble in carbon tetrachloride and chloroform, and it appeared stable upon heating to $115^\circ C$ for several hours since it neither formed volatile materials nor changed its physical appearance.

In one experiment a sample of 0.54 mmole of the hydrogen cyanide adduct of borazole which weighed 87.5 mg. was heated to $162^\circ C$ in a flask which was attached to a mercury manometer. The pressure increased in the reaction vessel until after two

hours the evolution of gaseous material ceased. It was found that 0.14 mmole of non-condensable gas had been formed. Upon separation of the hydrogen the rest of the volatile material was shown by an infrared spectrum in a gas cell to be a mixture of hydrogen cyanide and borazole which upon liquification recombined to form the white adduct discussed previously. The total amount of borazole and hydrogen cyanide could not be determined since some of it reacted to form the adduct when the hydrogen was fractionated from the mixture at low temperatures.

Reaction of borazole with deuterium sulfide   Attempts to exchange or react deuterium sulfide with borazole were made under various experimental conditions. In a sealed reaction flask of 50 cc. volume 0.17 mmole of borazole and 0.61 mmole of deuterium sulfide were allowed to remain at $-30^{\circ}C$ for five minutes with borazole in the liquid phase. In a bulb of 50 cc. volume 0.62 mmole of borazole was allowed to remain at room temperature for 12 hours with 1.25 mmole of deuterium sulfide. Finally, 0.17 mmole of borazole and 0.68 mmole of deuterium sulfide were heated at $103^{\circ}C$ for 55 minutes in a bulb of 50 cc. volume. In all cases both reactants were quantitatively recovered by distilling the reaction mixture through a $-95^{\circ}C$ bath which retained only the borazole. The mass spectrum of the recovered borazole was identical with that of borazole of natural isotopic composition; therefore,

no exchange had taken place.

<u>Reaction of borazole with deuterium oxide</u>   Into a
flask of 5 cc. volume were condensed 0.19 mmole of borazole
and 11.1 mmoles of deuterium oxide. The mixture was warmed
to $0^{\circ}C$ and allowed to remain at this temperature for 15-20
minutes. One third of the borazole was recovered when the
remaining reaction mixture was distilled through a $-45^{\circ}C$ bath
which trapped out water but permitted borazole to pass
through. The mass spectrum of the recovered borazole was
found to be identical with that of borazole of normal iso-
topic composition, and no peak above $m/e = 81$ was observed.

To test the possibility that an acid solution might
catalyze the exchange, a new run was made in the presence of
phosphoric anhydride for two to three minutes at temperatures
slightly above $0^{\circ}C$. Quantities of 0.18 mmole of borazole and
13.9 mmoles of deuterium oxide were used in this reaction.
Again the mass spectrum of the recovered borazole was clearly
that of unsubstituted borazole; hence, no exchange had taken
place.

Similarly, the possibility of a base catalyzed exchange
was investigated. Borazole, 0.25 mmole, and 10 mmoles of
deuterium oxide were allowed to react at $0^{\circ}C$ for two minutes
in the presence of 0.10 mmole of trimethylamine. The hydrol-
ysis of borazole by deuterium oxide had proceeded so exten-
sively under these conditions that no borazole could be re-

covered. The reaction was repeated with the same negative result.

Reaction of borazole with deuterated ethanol   Amounts of 0.22 mmole of borazole and 2.4 mmoles of deuterated ethanol were allowed to remain for five minutes at $-45^{\circ}C$. Unreacted borazole was recovered by distillation through a $-45^{\circ}C$ bath which retained only ethanol. The mass spectrum on a sample of the recovered borazole showed only mass peaks up to $m/e = 81$ indicating that no detectable exchange had occurred under the experimental conditions employed.

Reaction of borazole with deuterated acetylene   In a flask of 10 cc. volume 0.08 mmole of borazole and 0.28 mmole of deuterated acetylene were allowed to remain at room temperature for five minutes. Both compounds were quantitatively recovered from the reaction mixture by distillation through a $-112^{\circ}C$ bath which permitted only the acetylene to pass. The mass spectrum of the recovered borazole showed that no exchange had taken place.

In a similar experiment 0.23 mmole of deuterated acetylene and 0.09 mmole of borazole were heated in the gas phase to $80^{\circ}C$ for 30 minutes. No attempt was made to separate the mixture; however, the mass spectrum showed only the peaks of borazole of natural isotopic composition. Finally, a 0.19 mmole sample of borazole was reacted in a flask of 2 cc. volume with 2.25 mmoles of deuterated acetylene in the liquid

phase at $-50^{\circ}C$ at which temperature the equilibrium vapor
pressure of the acetylene is 5 atm. After the mixture stood
for 10 minutes, the reactants could be quantitatively recov-
ered. Again the mass spectrum indicated that no exchange had
taken place.

<u>Reaction between borazole and deuterium</u>   A sample of
0.05 mmole of borazole was heated with 1.41 mmoles of deuter-
ium in a bulb of 250 cc. volume for one hour at $200^{\circ}C$. A
mass spectrum of the recovered borazole showed mass peaks up
to $m/e = 84$; therefore, only three hydrogen atoms on the
borazole ring had undergone exchange. An infrared investi-
gation on the gaseous sample of recovered borazole clearly
indicated the disappearance of the B-H band at 3.9μ and the
appearance of a B-D band at 5.3μ.

Numerous similar experiments were carried out in an
attempt to observe the rate of deuteration of borazole. A
reaction vessel was prepared by attaching a 4 mm high-vacuum
stopcock to a flask of 125 cc. volume. The exact volume of
the flask was then determined by allowing a weighed amount of
carbon dioxide to expand into the flask on the high-vacuum
system. From the volume of the system and the pressure of
the carbon dioxide, the volume of the flask could be readily
calculated. A known amount of borazole, usually 0.05 mmole,
and 10 mmoles of deuterium were introduced into the flask
which was heated in a constant temperature bath at $127.5^{\circ}C$ for

time periods ranging from 10 minutes to 30 minutes. The flask
was then quickly chilled and the deuterium was pumped off at
liquid nitrogen temperature. The progress of deuteration was
followed by introducing samples of the recovered borazole
into the mass spectrometer at identical pressures and observ-
ing the change in relative intensity in peaks of highest mass,
$m/e = 82$ and $m/e = 83$. Great care was taken to keep varia-
tions in experimental procedure to a minimum, yet it was not
possible to obtain reproducible results.

In a second series of experiments the influence of sur-
face area on the rate of reaction was investigated. Identical
samples of borazole and deuterium were heated at $127.5^\circ C$ in
two flasks of equal volume, one filled with Pyrex glass wool
and one empty. Although reproducible results were not ob-
tained, it appeared that in all runs the reaction progressed
more slowly in the reaction vessel filled with glass wool.

An experiment to initiate the isotope exchange between
borazole and deuterium at room temperature with azomethane
present as a source of free radicals was not successful.

Reaction between borazole and deuterated diborane   In
a sealed glass vessel 0.11 mmole of borazole and 0.22 mmole of
deuterated diborane were allowed to stand at room temperature
in the gas phase for 30 minutes. The reactants were quanti-
tatively redovered by fractional distillation through a $-95^\circ C$
bath which retained only borazole. A mass spectrum of the

recovered borazole showed peaks up to m/e = 84 indicating that
exchange of three of the six hydrogens in the borazole mole-
cule had taken place. Infrared spectra indicated the appear-
ance of B-D bands at 5.3 μ and the disappearance of B-H bands
at 3.9 μ.

Reaction of borazole with sodium borohydride   A flask
of 5 cc. volume was charged with 2 mmoles of partially deuter-
ated sodium borohydride through a sidearm which was then seal-
ed off in a stream of dry nitrogen. Then, 0.31 mmole of bora-
zole was introduced, and the reaction flask was allowed to
stand for five hours at room temperature. A liquid phase of
borazole was present under these conditions. A mass spectrum
of the recovered borazole showed only mass peaks up to m/e =
81. Therefore, no exchange had taken place.

To test the possibility that the insolubility of sodium
borohydride in borazole might be responsible for the failure
to exchange, 0.31 mmole of borazole was allowed to interact
at room temperature with 2.0 mmoles of partially deuterated
sodium borohydride dissolved in 1 cc. of diglyme. About one
sixth of the borazole was recovered by fractional distilla-
tion of the reaction mixture through a -45°C bath which re-
tained the ether but permitted the borazole to pass. A mass
spectrum showed that borazole had not undergone isotopic ex-
change.

In another experiment the possibility of the interaction
of gaseous borazole with sodium borohydride at higher temper-
atures was checked. A sample of 0.18 mmole of borazole was

heated with 2.0 mmoles of partially deuterated sodium boro-hydride for three hours at 150-160°C. The mass spectrum of the borazole recovered from this reaction in which no non-condensable gas was found showed mass peaks up to m/e = 84. The appearance of a B-D band at 5.3μ in the infrared spectrum indicated that the hydrogen on the boron atoms in the borazole molecule were involved in the exchange.

Preparation of deuterated borazoles

Preparation of B-deuterated borazole   In a flask of 250 cc. volume 0.85 mmole of borazole and 5.1 mmoles of deuterium were heated at 200°C. After one hour the hydrogen-deuterium mixture was pumped off and 5.1 mmoles of fresh deuterium were introduced. The procedure was repeated a total of four times until the intensities of the mass peaks m/e = 84 and m/e = 83 did not change. From this was concluded that the exchange of hydrogen for deuterium on the boron atoms was com-plete. The borazole was then freed from possible decomposi-tion products by distillation through a -63.5°C bath into a -95°C cold bath. This process was repeated until the fraction in the -95°C bath (borazole) had a constant vapor pressure of 85.7 mm at 0°C. An infrared spectrum was recorded in a sodium chloride gas cell at 10 mm pressure (for spectrum see Figure 1 in the Discussion section).

For the purpose of comparing the mass spectrometric frag-mentation pattern of B-deuterated borazole with borazole of natural isotopic composition mass spectra of these were

recorded under identical conditions. Mass spectrometric data for the group of peaks of highest mass are presented in Table 1 for borazole and in Table 2 for B-deuterated borazole.

Preparation of perdeuterated borazole   Perdeuterated borazole was prepared from deuterated diborane and deuterated ammonia by the method that was originally developed by Stock and Pohland for the preparation of borazole (52). The source and purity of these reagents has been previously discussed.

Amounts of 1.98 mmoles of deuterated borazole and 3.95 mmoles of deuterated ammonia were frozen on the walls of a flask of 500 cc. volume, which was then permitted to warm slowly to room temperature over a period of 12 hours. Unreacted reagents were pumped off from the non-volatile

Table 1. Mass spectrometric data for borazole

Scale divisions	Relative intensities in percent	Mass (m/e)
1050	34.3	81
3060	100.0	80
1926	63.1	79
658	21.5	78
328	10.7	77
265	8.7	76
125	4.1	75
32	1.0	74

Sensitivity for base peak in scale divisions

per micron pressure	80	49.8
for butane	43	95.2

Table 2. Mass spectrometric data for B-deuterated borazole

Scale divisions	Relative intensities in percent	Mass (m/e)
972	41.2	84
822	34.8	83
2364	100.0	82
1650	69.8	81
480	20.3	80
197	8.3	79
174	7.4	78
143	6.1	77
116	4.9	76
56	2.4	75
17	0.7	74

Sensitivity for base peak in scale divisions

per micron pressure   82   38.5

for butane   43   95.2

addition product, and the sealed flask was now rapidly heated to 185°C for 2 hours. The borazole was recovered from the reaction mixture by the fractional distillation and condensation procedure described in the previous section. The purified product had a vapor pressure of 87.5 mm at 0°C.

Preparation of N-deuterated borazole   N-deuterated borazole was best prepared by the "back exchange" of perdeuterated borazole with hydrogen. A sample of 0.40 mmole of perdeuterated borazole was heated to 200°C with 5 mmoles of hydrogen for one hour. This procedure was repeated with fresh portions of hydrogen until the mass spectrum of the

borazole showed no further decrease in the relative intensities of the two highest mass peaks. Infrared spectra of N-deuterated borazole and perdeuterated borazole were recorded at 10 mm pressure and are found in the Discussion section, Figure 2 and Figure 3, respectively.

Mass spectrometric data for the group of peaks of highest mass are shown in Table 3 for N-deuterated borazole, and in

Table 3.   Mass spectrometric data for N-deuterated borazole

Scale divisions	Relative intensities in percent	Mass (m/e)
3900	28.9	84
11850	87.8	83
13500	100.0	82
7950	58.9	81
2595	19.2	80
1095	8.1	79
1010	7.5	78
865	6.4	77
760	5.6	76
505	3.7	75
218	1.6	74

Sensitivity for base peak in scale divisions

        per micron pressure   82   26

        for butane   43   109

Table 4 for perdeuterated borazole. Both compounds were impure with respect to hydrogen since pure samples of deuterated ammonia and deuterated diborane from which these compounds were formed were not available.

Table 4. Mass spectrometric data for perdeuterated borazole

Scale divisions	Relative intensities in percent	Mass (m/e)
1845	39.2	87
1680	35.8	86
4700	100.0	85
3600	76.5	84
1155	24.6	83
201	4.3	82
255	5.4	81
198	4.2	80
231	4.9	79
150	3.2	78
156	3.3	77
96	2.0	76
33	0.6	75
6	0.1	74

Sensitivity for base peaks in scale divisions

per micron pressure   85   38

for butane   43   109

Miscellaneous reactions of borazole

Reaction of borazole with anhydrous chloral   Samples
of 0.38 mmole of borazole and 33 g. of anhydrous chloral, the
preparation of which was described earlier, were sealed into
a flask of 100 cc. volume and heated over a steam bath for 30
minutes. By this time the contents of the reaction flask
appeared gelatinous, and some gas non-condensable in a liquid
nitrogen bath was in evidence. About 25% of the borazole was
recovered; however, chloroform which should have been present
had a formylation reaction (6) occurred was not found. The
absence of chloroform was ascertained by an infrared spectrum
taken of the volatile contents of the reaction flask. The
reaction between borazole and anhydrous chloral was conse-
quently not further pursued.

Reaction of borazole with decaborane   A sample of
3.24 mmoles of borazole was frozen in the vacuum system on
1.03 mmoles of decaborane. The reaction flask was warmed and
kept at room temperature for 10 minutes. A liquid phase of
borazole was present in which the decaborane did not appear
to dissolve. Practically all the borazole, 3.20 mmoles, was
recovered and had a vapor pressure of 87 mm at $0^{\circ}C$ as com-
pared to 85.5 mm at $0^{\circ}C$ for pure borazole. The remaining
material in the flask had increased in weight by 3.1 mg.

Reaction of borazole with glacial acetic acid   The
reaction between borazole and acetic acid was highly exo-

thermic, and when an excess of acetic acid was used a viscous reaction product usually resulted in which the apparent molar ratio of borazole to acetic acid varied from 1:4 to 1:5.7. Upon heating the reaction product to $150^{\circ}C$ for 30 minutes, acetic acid was given off and crystals formed in the cold parts of the flask. These crystals were deliquescent in air, insoluble in ether, but soluble in chloroform and had a melting point of $82^{\circ}C$. The odor and infrared spectrum were identical to that of acetamide for which a melting point of $81^{\circ}C$ has been reported.

When an excess of borazole was used, the molar ratio of borazole to acetic acid decreased to 1:1.9, and a white product remained in the reaction flask. Upon heating to $90^{\circ}C$ for 90 minutes, this material liberated borazole and ammonia which were identified mass spectrometrically and by infrared spectra.

It was found that the reaction between borazole and acetic acid could be moderated by dissolving the acid in anhydrous diethyl ether and then adding borazole to the solution. A quantity of 19.52 mmoles of acetic acid was dissolved in 50 cc. of ether contained in a reaction flask equipped with a magnetic stirrer and a side arm. While the contents of the flask were kept under dry nitrogen, 5.84 mmoles, 0.4733 g., of borazole which was weighed by difference were slowly introduced through the sidearm by means of a syringe. After

one half of the reagent had been added, a white precipitate formed. The stirring was continued for 30 minutes after the reaction was complete. After 8 hours, the reaction mixture was filtered and washed with ether in a carefully prepared dry box. The filtrate and ether washings were treated with 45 cc. of water, and the ether was distilled from a flask to which was attached a reflux condenser. The aqueous solution was then titrated with 0.1N sodium hydroxide using phenolphthalein as the indicator. The end point, however, was not sharp and 1.95-2.1 equivalents of base were used to neutralize the excess acetic acid.

No suitable solvent was found for the recrystallization of the acetic acid adduct of borazole. The compound reduced silver nitrate in aqueous solution, and though readily attacked by water, hydrolyzed completely only in strong acid solution.

A boron and a nitrogen analysis were performed on the impure product. Analysis calculated for $B_3H_3N_3H_3 \cdot 3CH_3COOH$: B, 12.5; N, 16.2; Found: B, 10.5; and N, 12.5. A molecular weight determined cryoscopically in glacial acetic acid gave a value of 236 as compared to 260.7 for the acetic acid adduct of borazole, $B_3H_3N_3H_3 \cdot 3CH_3COOH$.

DISCUSSION

Reactions of B-Trichloroborazole

Studies of substitution reactions on B-trichloroborazole appear to indicate that a replacement of the halogen by other inorganic anions is possible. In contrast to this, trichlorobenzene, which is isosteric and isoelectronic to trichloroborazole, is not known to undergo such substitution under these conditions.

A substitution on B-trichloroborazole is best achieved by using an inorganic salt which is readily soluble in the organic solvent chosen to dissolve the trichloroborazole; however, the resulting inorganic halide should be highly insoluble. In the reactions of silver nitrate and potassium thiocyanate with trichloroborazole these conditions were met. The reaction of silver cyanide with trichloroborazole proceeded less readily because of the insolubility of the cyanide salt in acetonitrile. The silver chloride formed, however, appeared to be even less soluble, and the reaction could be completed by agitating the reaction mixture with glass beads which renewed the surface of any silver cyanide coated with precipitated silver chloride. Potassium cyanate was also found to be rather insoluble in acetonitrile, and presumably the concentration of available cyanate ions was not sufficient to exceed the solubility product for potassium chloride

in acetonitrile.

Magnesium bromide, mercuric iodide and aluminum bromide failed to react with trichloroborazole in 1,2-dimethoxyethane, methyliodide and toluene, respectively, even though these reagents, as well as trichloroborazole, were readily soluble in each particular solvent. It may be argued that in these solvents a dissociation of the inorganic salt into ions is not favored so that a reaction was not likely to occur. It is somewhat surprising to note that magnesium perchlorate, as well as lithium bromide, which are both readily soluble in acetonitrile, also failed to react with trichloroborazole in this solvent, especially since lithium chloride is reported to be only slightly soluble in acetonitrile (1).

The nitration reaction of trichloroborazole with silver nitrate apparently lead to the expected, though highly unstable, trinitratoborazole. The ease of elimination of nitrogen dioxide above $0^{\circ}C$ suggests that the nitrate group is attached to the boron atoms by means of one of its oxygen atoms. The explosion of an ether extract of a toluene trinitratoborazole mixture cannot be adequately explained. A smell of nitrobenzene was evident after the explosion which suggests that a nitration of toluene might have occurred under the experimental conditions. A nitration of the benzene ring in this fashion would be interesting since its direct nitration by known methods requires somewhat more drastic experi-

mental conditions, such as warming with fuming nitric acid.
A repetition of the reaction of trichloroborazole with silver
nitrate in the presence of sufficient benzene or toluene to
prevent possible formation of trinitro compounds should reveal
whether the ether adduct of trinitratoborazole can act as a
nitrating agent.

The possibility of a reaction of the ring nitrogen in
trichloroborazole with anhydrous chloral was contemplated in
view of the success of the formylation of various amines such
as butylamine, ethylenediamine, piperidine, benzylamine and
others (6). Furthermore, the desired product could serve as
an intermediate in the convenient formation of N-trimethyl-
borazole which would be obtained by the reduction of the
formyl derivative with lithium aluminum hydride.

The desired formylation reaction, however, did not occur
which may be explained by the following argument. The reac-
tion of chloral with amines proceeds by an electrophilic
attack of the positive carbon of the carbonyl group on the
free pair of electrons on the nitrogen atom of the amine. One
would expect this reaction to proceed most readily for amines
of greatest basicity. The amines mentioned above are indeed
strong ones with pK values ranging from 2.8 for piperidine to
4.7 for benyzlamine. It appears then probable that the
nitrogen atoms in the borazole skeleton are not of sufficient
basicity to permit a similar reaction with chloral.

The chemical analysis on the product obtained from the reaction between pyridine and trichloroborazole seems to indicate the formation of a 1:3 adduct in which the pyridine molecules may be associated with the electron deficient boron atoms of the borazole nucleus. Alternately, it may be suggested that the pyridine forms a hydrochloride leaving the B-N skeleton, $(BN)_x$, of borazole. Infrared studies in Nujol and potassium bromide pellets were unsuccessful in gaining information on the nature of the product. However, since pyridine hydrochloride is reported to melt at $82^{\circ}C$, the relatively high melting point range of $145-150^{\circ}C$ for the product seems to exclude the presence of pyridine hydrochloride.

It is interesting to note that pyridine and its methyl derivatives, which are rather weak bases, pK_B approximately 9, react so readily with trichloroborazole while triethylamine and tri-n-butylamine which are very strong bases, $pK_B = 3.7$ and $pK_B = 3.3$, respectively, were not observed to react appreciably. Triethylamine, for example, reacted only very slowly over a period of four hours with a benzene solution of trichloroborazole. Similarly, tri-n-butylamine which was used in the reduction of trichloroborazole with sodium borohydride to absorb the diborane formed did not lower the yield of borazole ordinarily obtained in the absence of the amine.

Since the base strength appears not to be a determining factor in the compound formation, explanation for the differ-

ence in behavior may lie in the steric requirements necessary to permit approach of the base to the boron atoms. These are more favorable for pyridine than for triethylamine or especially tri-n-butylamine. A test for this assumption would be provided by the use of a hindered base such as 2,6-dimethyl-N,N-dimethyl aniline, the structure of which is as found below:
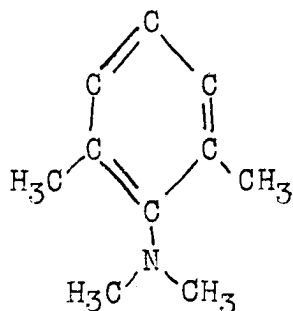
This base readily accepts a proton but for steric reasons will not coordinate with boron (11). In some preliminary experiments 2,6-dimethyl-N,N-dimethyl aniline was added to solutions of trichloroborazole in toluene and neither warming nor the formation of a precipitate was observed. The failure of this base to react with trichloroborazole would seem to support the reasoning presented above.

It has already been mentioned that borazole adds three moles of HX (HCl, HBr, HOR, and HOH) to form addition products which are reported to eliminate hydrogen upon heating (61). Furthermore, if the heating of, for example, the hydrogen bromide adduct of borazole is performed in the presence of water, the formation of the compound B-tribromotrihydroxy-

borazole, $B_3Br_3(OH)_3N_3H_6$, is claimed (61). In principle then it appears possible to synthesize cyclohexane type derivatives of borazole in which two inorganic groups are attached to the boron atoms. In this investigation such a synthesis was achieved by reacting one mole of monochloroborazole with three moles of hydrogen chloride. In the resulting adduct, two chlorine atoms were presumably attached to one boron atom in the borazole nucleus:
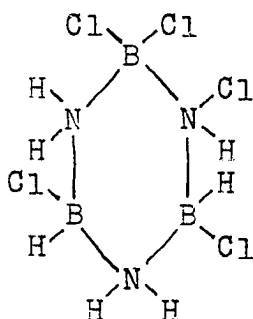
It may well be that the preparation of compounds in which all the boron atoms have two inorganic groups attached is considerably more difficult by this method.

By thermal elimination of two moles of hydrogen from the hydrogen chloride adduct of monochloroborazole, a partially unsaturated borazole should result:
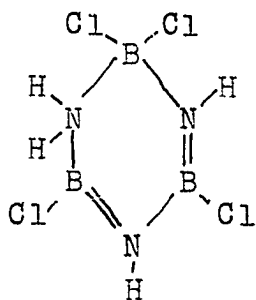
or alternately by elimination of one mole of hydrogen chloride and two moles of hydrogen trichloroborazole would be obtained. However, the thermal decomposition of the hydrogen chloride adduct of monochloroborazole yielded only 4% of the total expected hydrogen before practically all of the solid had disappeared from the heated flask. In the cold trap volatile products were observed which were not further identified.

It is interesting to compare this behavior of the hydrogen chloride adduct of monochloroborazole at higher temperatures with that of an identical quantity of the hydrogen chloride adduct of borazole. It is seen from the described experimental results that about 18% of the total hydrogen expected from the dissociation of one mole of adduct into three moles of hydrogen was released. The presence of a non-volatile solid left in the flask appears to further indicate that the thermal decomposition of the two adducts proceeds along different paths.

The investigations of the reduction of trichlorobroazole were undertaken with the hope to find a convenient way to prepare borazole which would require only conventional equipment used in organic synthetic work. In view of the successful reduction of boron trichloride by monosilane in the presence of azomethane (43) it was hoped that similarly trichloroborazole could be reduced to borazole by silane compounds. Phenylsilanes were used for this because they are

stable in air and are at the same time good solvents for tri-
chloroborazole. All these reactions failed in the absence as
well as in the presence of free radical initiators presumably
because of the lack of hydridic character of the silicon
hydrogen bonds which may be necessary to facilitate the attack
on the boron atoms.

Sodium hydride has not been observed to reduce trichloro-
borazole in diglyme solution; however, should diborane react
with sodium hydride in diglyme to form sodium borohydride,
the reduction of trichloroborazole could be performed by
sodium hydride in the presence of catalytic quantities of
sodium borohydride. This would possibly also make any pre-
cautions to handle the liberated diborane unnecessary.

The fact that only traces of borazole were isolated from
these reactions appears to indicate that the possible regenera-
tion of sodium borohydride from diborane and sodium hydride
does not occur. It was decided to attempt to use an amine
to complex the diborane formed in the reduction step. The
suitable amine should neither react with the reactants nor
products involved in the reduction. It should completely
complex the diborane formed, and should not interfere with
the isolation of the borazole. Tri-n-butylamine does not
appear to undergo reaction other than complexing of diborane;
furthermore, its high boiling point of $214^{\circ}C$ permits its
facile separation from borazole. The amine was entirely

effective in preventing the escape of diborane from the reaction mixture, and no precautions other than avoiding hydrolysis of borazole had to be taken. For large scale preparation the recovery of the amine borane and reconversion to free amine and sodium borohydride by treatment with sodium hydride might be considered (31). The net reaction in that case would correspond to reduction of trichloroborazole with sodium hydride.

Reactions of Borazole

The possibly weakly basic properties of the nitrogen in the borazole nucleus which have been already discussed for the reaction of B-trichloroborazole with chloral are probably also responsible for the failure of the reaction of chloral with borazole.

It was thought possible that decaborane which possesses two acidic hydrogens in the 6,9 position might react with borazole analogous to the addition of compounds of the type HX to borazole previously described. This reaction should be repeated in the presence of a suitable solvent.

The reaction of acetic acid with borazole lead to a reaction product that could not be readily purified. Since only small amounts were available, recrystallization from acetic acid, in which it is very soluble, was not attempted. The stoichiometry, analysis and molecular weight determina-

tions on the crude product appear to agree with the formation of an adduct containing three moles of acetic acid per mole of borazole in analogy to numerous other similar adducts reported in this work and in the literature (60, 61).

In the discussion of isotopic exchange reactions of borazole exchange involving hydrogen on the nitrogen atoms may be considered first. At low temperatures in the liquid phase, rapid reaction and exchange were observed with ammonia; while in the gas phase at room temperature, slow reaction and no exchange occurred. This appears to support an ionic mechanism of exchange for which at least two possible paths can be postulated. Protons might be reversibly ionized from the nitrogen atoms in the borazole molecule to form ammonium ions with the ammonia present, and with a nearly statistical probability either a proton or a deuteron will be recovered by the borazole ion. Alternately, one may consider the ammonium ion formed in the autoionization of ammonia as undergoing exchange with the borazole present. Presumably these exchange reactions are extremely fast and take place before an adduct between borazole and ammonia can be formed (61).

Deuterium chloride was found to react and exchange with borazole in the liquid as well as in the gas phase. A reasonable mechanism for the exchange can be postulated if one associates it with the mechanism of adduct formation. The addition of the first molecule of deuterium chloride may proceed

by an attack of the deuterium on the nitrogen to form an intermediate from which the adduct can be formed by an intramolecular nucleophilic attack of the chlorine on the boron atom. It is conceivable that either or both the intermediate and the adduct may revert to the starting material. Since borazole was not found to exchange with the deuterium chloride adduct itself, it may be concluded that at least the addition of a third molecule of deuterium chloride is not reversible.

Deuterium cyanide was found to react and exchange with borazole only in the liquid phase suggesting that an ionic mechanism is involved which is facilitated by the high dielectric constant of deuterium cyanide.

Isotopic exchange of deuterium oxide and deuterated ethanol with borazole was not observed to take place even though it is known that both water and ethanol will react with borazole to form addition compounds (61). Apparently no reversible steps are involved in the addition reaction that could facilitate isotopic exchange. The presence of phosphoric acid did not appear to catalyze exchange between deuterium oxide and borazole. With trimethylamine present the hydrolysis of borazole proceeded so rapidly at $0^{\circ}C$ that no borazole could be recovered.

The failure of deuterated acetylene and deuterium sulfide to react or exchange with borazole in the gas phase as well as the liquid phase may be attributed to the lack of acid char-

acter of the deuterium atoms in these compounds and their exceedingly low autoionization in the liquid phase.

The hydrogens on the boron atoms in borazole were found to undergo exchange with deuterium at elevated temperatures. Considerable effort was made to study the kinetics of this reaction by observing mass spectrometrically the progress of the deuteration. Results were inconsistent and did not lead to a ready explanation of the mechanism. It appears, however, that an increase in surface area in the reaction vessel reduced the extent of deuteration. This behavior is characteristic of some free radical reactions; however, a deuteration of borazole at room temperature in the presence of azomethane as a source of methyl radicals did not take place.

The exchange of diborane with borazole which takes place at room temperature can be readily explained by the formation of an intermediate involving a hydrogen bridge between borazole and diborane. In a subsequent step the cleavage will occur which either leaves a hydrogen or a deuterium atom on the borazole.

Deuterated sodium borohydride was found only to exchange at 150-160°C. Apparently, the intermediate facilitating the exchange is favored at high temperatures. It is unlikely that trace amounts of hydrogen that escaped detection catalyzed the exchange since both borazole as well as sodium borohydride are thermally stable at 150°C.

The preparation of various deuterium substituted bora-
zoles need not be commented on. It should be noted, however,
that an alternate route of synthesis of nitrogen or boron
deuterated borazoles by reacting deuterated ammonia with
diborane or ammonia with deuterated diborane using Stock's
method of synthesis (52) is not feasible since the hydrogen
formed can obviously exchange with borazole at the reaction
temperature. Partially deuterated borazole with substitution
on the boron as well as on the nitrogen atoms will conse-
quently result.

The infrared spectra of deuterated borazoles and borazole
are recorded in Figures 1, 2, 3 and 4. The shift of the N-H
and the B-H stretching frequencies at 2.8μ and 3.9μ, re-
spectively, can readily be seen. The bands at 13.9μ and
10.9μ which were assigned by Price and co-workers to N-H,
B-H in plane bending frequencies (37) are similarly shifted
to higher wavelengths. Thus, in borazole the bands at 13.9μ
appear to be associated with N-H bending while the bands at
10.9μ appear to represent B-H bending frequencies. The
absorption band at 7μ which is associated with B-N deforma-
tion in the ring is slightly displaced to 7.1μ for per-
deuterated borazole. Even though the shift increases as
expected from borazole to perdeuterated borazole, it may be
possible that it reflects only the inconsistency of the
instrument used to record the spectrum.

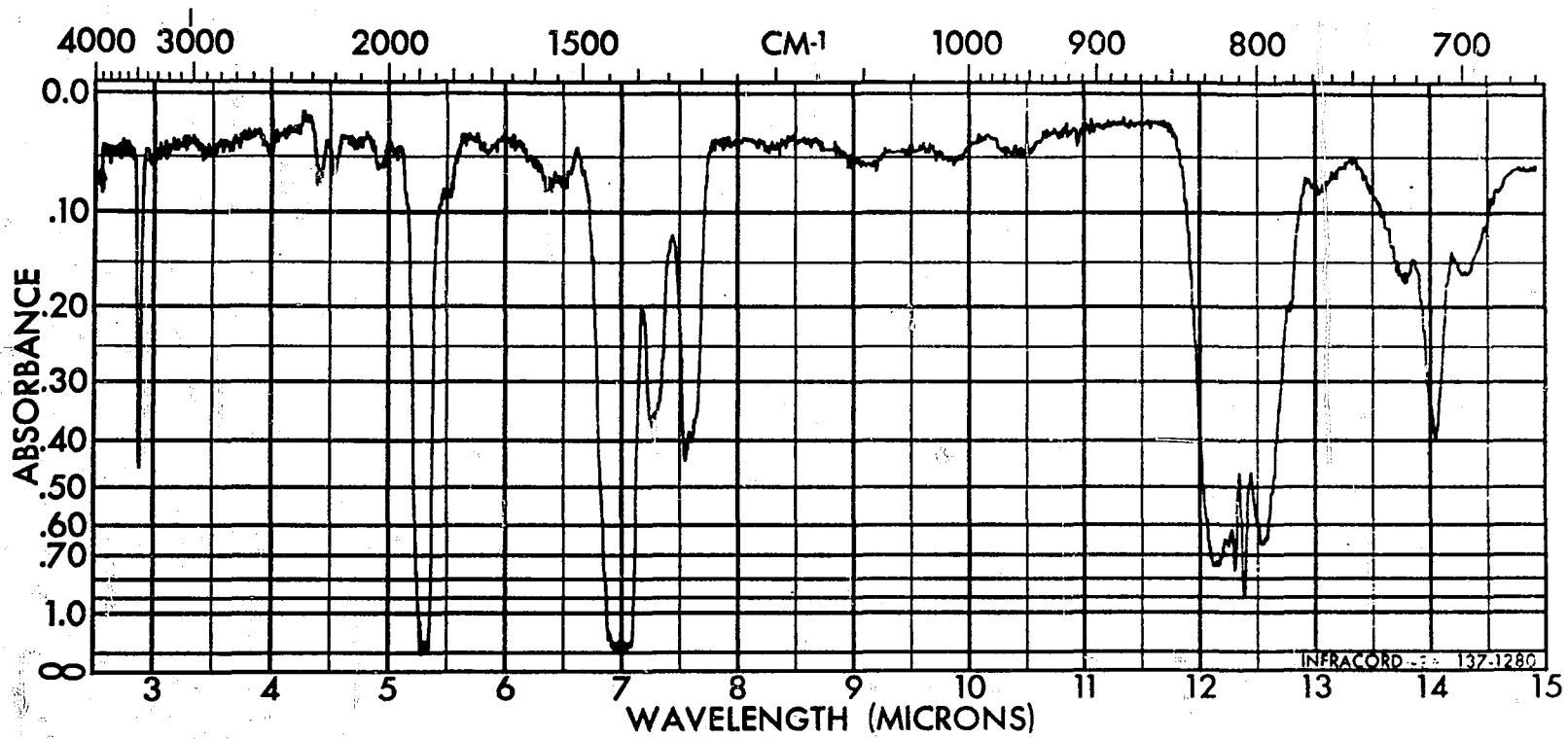Figure 1. Infrared spectrum of B-deuterated borazole

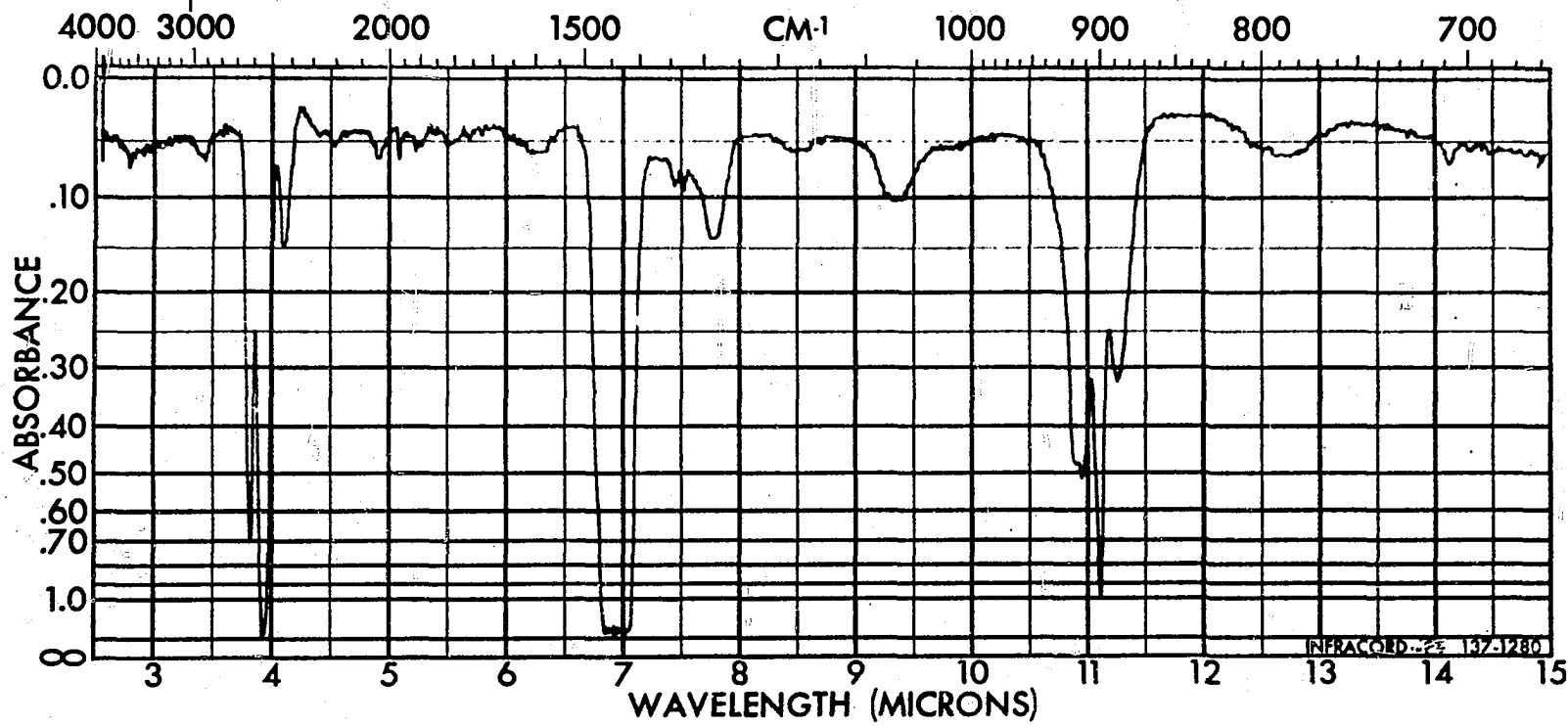Figure 2. Infrared spectrum of N-deuterated borazole

Figure 3.   Infrared spectrum of perdeuterated borazole
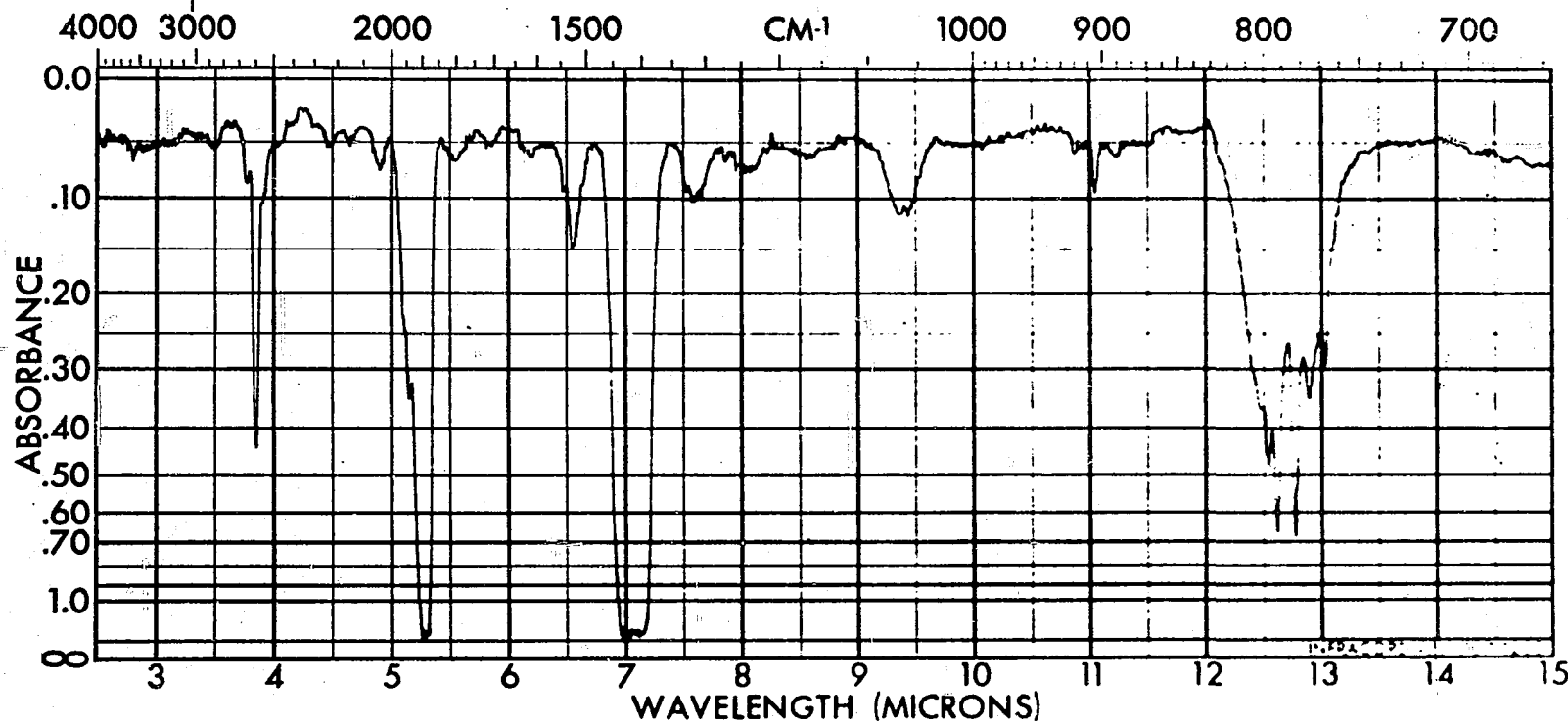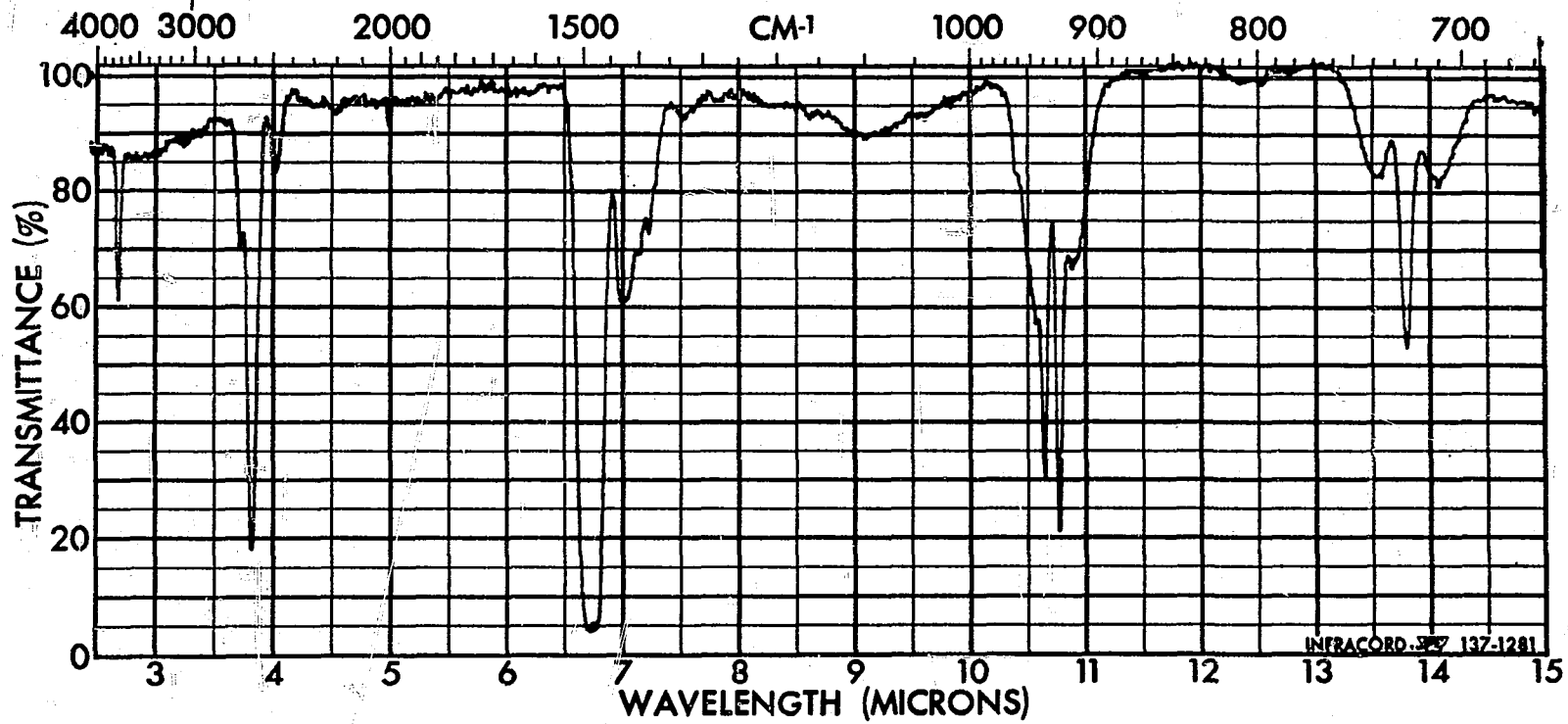
WAVELENGTH (MICRONS)

Figure 4. Infrared spectrum of natural borazole

The comparison of the group of peaks of highest mass
observed for the mass spectra of borazole and B-deuterated.
borazole is quite interesting. For B-deuterated borazole
the peak of highest relative intensity is two mass units below
the parent peak; for borazole the most intense peak imme-
diately follows the parent peak. It appears that in the first
ionization step of the borazole molecule in the mass spectro-
meter the hydrogen attached to the boron is abstracted first.
A calculation will serve to explain this in detail.

In the spectrum for B-deuterated borazole the peak of
mass 83 and 34.8% relative intensity, neglecting nitrogen
isotopes because of their small abundance, is contributed by
two species: $B_3^{11}D_3N_3H_2^+$ and $B_1^{10}B_2^{11}D_3N_3H_3^+$. If one sets
the probability of the occurence of $B^{10} = X$ and $B^{11} = 1-X$,
one obtains the following probability expressions for the
various combinations of boron atoms in the borazole molecule:

$$B_3^{10} = X^3$$
$$B_2^{10}B_1^{11} = 3X^2(1-X)^2$$
$$B_1^{10}B_2^{11} = 3X(1-X)^2$$
$$B_3^{11} = (1-X)^3$$

Although the natural abundance of B^{10} and B^{11} is reported as
18.8% and 81.2%, respectively (26), the ratio of 20% to 80% is
preferred for mass spectrometric work with compounds contain-
ing boron hydrogen bonds since such a ratio results in a min-
imum residue in calculating monoisotopic spectra (15, 58).

Substituting these values into the probability expressions one obtains: $B_3^{10} = 0.008$, $B_2^{10}B_1^{11} = 0.096$, $B_1^{10}B_2^{11} = 0.384$, $B_3^{11} = (1-X)^3 = 0.512$; and, therefore,

$$\frac{B_1^{10}B_2^{11}}{B_3^{11}} = 0.750.$$

One can now easily calculate the contribution of the $B_1^{10}B_2^{11}D_3N_3H_3^+$ species to the 83 peak in B-deuterated borazole. The height of the 84 peak representing only the species $B_{11}^{3}D_3N_3H_3^+$ is 972 units so that $972 \times 0.75 = 729$ of the 822 units of the 83 peak are due to the $B_1^{10}B_2^{11}D_3N_3H_3^+$ species. This means that 89% of the 83 peak must be attributed to the parent species, $B_1^{10}B_2^{11}D_3N_3H_3^+$, and only 11% to the $B_3^{11}D_3N_3H_3^+$ species. One is now able to calculate the contribution of the different species to the peak heights for the next lower m/e values by comparing the spectrum of borazole with that of B-deuterated borazole both of which were obtained under comparable conditions. The values of relative intensities of the species contributing to the 79, 80, and 81 peaks for borazole and the 82, 83, and 84 peaks for B-deuterated borazole are shown in Tables 5 and 6, respectively. The relative intensities are referred to the most abundant species, $B_3^{11}D_2N_3H_3^+$ and $B_3^{11}H_2N_3H_3^+$. As was shown, the contribution of $B_3^{11}D_3N_3H_2^+$ to the 83 peak of B-deuterated borazole could be easily determined. The ratio of

Table 5. Mass spectrum of borazole, $B_3H_3N_3H_3$ (mass 79-81)

Mass	Specie	Scale divisions per species	Scale divisions per peak	Relative intensity
81	$B_3{}^{11}N_3H_6{}^+$	1050	1050	48.5
80	$B_2{}^{11}B_1{}^{10}H_3N_3H_3{}^+$	788		36.3
	$B_3{}^{11}H_2N_3H_3{}^+$	2172	3060	100.0
	$B_3{}^{11}H_3N_3H_2{}^+$	101		4.7
79	$B_2{}^{10}B_1{}^{11}H_3N_3H_3{}^+$	197		9.1
	$B_2{}^{11}B_1{}^{10}H_3N_3H_2{}^+$	76	1926	3.5
	$B_2{}^{11}B_1{}^{10}H_2N_3H_3{}^+$	1630		75.0
	$B_3{}^{11}H_2N_3H_2{}^+$	23		1.1

$B_3{}^{11}D_3N_3H_2{}^+/B_3{}^{11}H_3N_3H_2{}^+ = 93/972 = 0.096$ then permitted the
estimation of the contribution of the $B_3{}^{11}H_3N_3H_2{}^+$ species to
the 80 peak of borazole, $B_3H_3N_3H_3$, which amounts to 101 scale
divisions. It is thus seen that only 4.4% of the total
$B_3{}^{11}N_2H_5{}^+$ species in the mass spectrometer are contributed by
the species which has lost a hydrogen atom from the nitrogen,
$B_3{}^{11}H_3N_3H_2{}^+$; while 95.6% is contributed by $B_3{}^{11}H_2N_3H_3{}^+$.
Similarly, the ratio $B_3{}^{11}H_2N_3H_3{}^+/B_3{}^{11}H_3N_3H_3{}^+ = 2172/1050 =$
2.069 allowed to calculate the contribution of $B_3{}^{11}D_2N_3H_3{}^+$ to
the 82 peak of B-deuterated borazole.

It should be noted that in these calculations the effect

Table 6. Mass spectrum of B-deuterated borazole, $B_3D_3N_3H_3$ (mass 82-84)

Mass		Scale divisions per species	Scale divisions per peak	Relative intensity
84	$B_3{}^{11}D_3N_3H_3{}^+$	972	972	48.3
83	$B_3{}^{11}D_3N_3H_2{}^+$	93	822	4.6
	$B_2{}^{11}B_1{}^{10}D_3N_3H_3{}^+$	729		36.1
82	$B_2{}^{10}B_1{}^{11}D_3N_3H_3{}^+$	183	2364	9.1
	$B_2{}^{11}B_1{}^{10}D_3N_3H_2{}^+$	70		3.5
	$B_3{}^{11}D_3N_3H^+$	100		5.0
	$B_3{}^{11}D_2N_3H_3{}^+$	2011		100.0

of deuterium present in the molecule upon the fragmentation pattern of borazole was disregarded. Since the contribution of the $B_3H_3N_3H_2{}^+$ species in borazole was calculated from the experimentally determined fragmentation pattern of B-deuterated borazole, $B_3D_3N_3H_3$, it may be asked whether the presence of a deuterium instead of a hydrogen on the boron atom will not influence the ionization of a hydrogen from the neighboring nitrogen atom. While a considerable isotope effect may be expected to influence the probability of breaking a B-H versus breaking a B-D bond or an N-H versus a N-D bond it is unlikely that the presence of a B-D instead of a B-H bond will

significantly influence the ionization of a hydrogen from the nitrogen atom.

Further examination of the relative tendency to ionize off the first hydrogen from the nitrogen or boron atoms can be carried out by comparing the 83 peak in the mass spectrum of N-deuterated borazole with the 83 peak in the spectrum of B-deuterated borazole. Unfortunately, a sample of mass spectrometrically pure N-deuterated borazole could not be prepared.

Problems in the investigation of chemical reactions of borazole and its halogen derivatives are plentiful. More inorganic substitution reactions, similar to those presented previously, may be carried out. However, the scope of such reactions would seem rather limited because of the low solubility of inorganic salts in organic solvents. The reactions of metal organic compounds with trichloroborazole would offer more opportunities. For example, sodium acetylide may be expected to form an acetylene compound and sodium chloride. Using monochloroborazole and disodium acetylide one may obtain a compound composed of two borazole rings linked by one acetylene group. Further investigation of cyclopentadiene reactions with B-trichloroborazole or borazole itself may not, as some preliminary experiments seem to indicate, lead to the isolation of borazole derivatives themselves but perhaps to borazole ring fragments containing cyclopentadiene

rings. The possibility of a reaction of trichloroborazole with decaborane may also be explored. The monosodium salt of decaborane, $B_{10}H_{13}Na$, could be expected to react with trichloroborazole to form sodium chloride and a borazole derivative of decaborane. Should this sodium salt reduce trichloroborazole rather than undergo a substitution, it would be interesting to determine the remaining decaborane fragments. Alternately by choosing a suitable solvent, trichloroborazole may react directly with decaborane which has at least two acidic hydrogens. Liberation of hydrogen chloride and the formation of a decaborane derivative of borazole may possibly result.

One interesting problem in line with the current interest in thermally stable inorganic polymers would be the synthesis of two dimensional or three dimensional systems of borazole nuclei attached to each other.

In connection with this investigation of the decomposition of borazole at room temperature which leads to clear syrupy as well as solid colorless products upon standing for several months should be interesting. It may well be possible that compounds composed of condensed borazole rings may be isolated. The naphthalene analog of borazole has already been observed in a pyrolysis study of borazole (34).

The chemistry of borazole itself should be further explored. The kinetics of the hydrogen isotope exchange with

deuterated diborane can be studied by infrared techniques.
Also the kinetics of the B-methylation of borazole by boron
trimethyl are not known. A novel methylation of borazole may
be attempted with diazomethane in analogy to the reaction of
trichloroborazole with diazomethane at low temperatures which
lead to a chloromethyl derivative (55). Another reaction
based upon the hydridic character of the boron hydrogen bond
may occur between borazole and dimethylamine leading to a
B-tri(N,N-dimethyl) borazole.

Further investigation of the cyclohexane type adducts
of borazole seems warranted especially since borazole is now
readily available. Infrared studies should yield more informa-
tion on the nature of these adducts and new compounds may pos-
sibly be synthesized from these adducts. The failure of
direct hydrogenation of borazole to a cyclohexane analog has
been tentatively explained by the instability of the result-
ing molecule (61). A reduction of the hydrogen chloride
adduct of borazole with a suitable reducing agent such as
sodium borohydride may yet lead to $B_3N_3H_{12}$ which is similar
to the compound $B_3H_6N_3H_3Me_3$ prepared recently from diborane
and methylamine (5).

Problems most challenging in the chemistry of the
borazole ring are the replacement reactions which only involve
the ring nitrogen. Such previous attempts to observe reactions
only on the nitrogen in the borazole ring have failed.

SUMMARY

The study of substitution reactions of B-trichloroborazole with inorganic salts in suitable organic solvents has resulted in the synthesis of B-trithiocyanatoborazole and B-tricyano-borazole. A compound presumed to be B-trinitratoborazole was found to decompose above $0^\circ C$ to form nitrogen dioxide and un-identified solid products. Other substitution reactions with lithium bromide, mercuric iodide, aluminum bromide, potassium cyanate, magnesium bromide, magnesium perchlorate and sodium or thallium salts of cyclopentadiene failed to produce new compounds either because no reaction took place or decomposi-tion of the products occurred. Attempts to prepare a N-formylborazole by reacting borazole or B-trichloroborazole with anhydrous chloral failed. The reaction of pyridine with B-trichloroborazole lead to a 1:3 adduct, $B_3Cl_3N_3H_3 \cdot 3pyridine$, in which the pyridine is presumably attached to the boron atoms. The hydrogen chloride adduct of monochloroborazole was prepared, and its thermal stability was compared to that of the hydrogen chloride adduct of borazole itself.

Numerous experiments were carried out in an attempt to find a procedure which avoids the liberation of the highly toxic and explosive diborane in the reduction of B-trichloro-borazole to borazole. Reductions with sodium hydride in the presence of catalytic quantities of sodium borohydride failed. Similarly, the reduction of B-trichloroborazole with organo

silanes in the presence as well as in the absence of free
radicals was unsuccessful. The reduction of B-trichloro-
borazole occurred readily in diglyme with sodium borohydride
in the presence of tri-n-butylamine which entirely complexed
the diborane formed. Yields of 46% were achieved by this
method. Borazole was found to add three moles of acetic acid
per mole of borazole to give a solid adduct, presumably sim-
ilar to other borazole adducts reported earlier in the litera-
ture. A reaction between decaborane and borazole in the ab-
sence of a solvent was not observed.

The isotopic exchange of borazole with various compounds
containing deuterium was studied. Deuterated ammonia, deuter-
ium chloride, and deuterium cyanide were found to exchange
with hydrogen on the nitrogen atoms in borazole. No exchange
was observed between borazole and deuterated ethanol and
deuterium oxide. No exchange and no chemical reactions were
detected with deuterium sulfide, deuterated acetylene, and
deuterated phosphine. Deuterium, deuterated diborane and
deuterated sodium borohydride were found to exchange with the
hydrogen on the boron atoms in borazole. Possible mechanisms
for the exchange reactions are discussed. Various deuterated
borazoles were synthesized and their infrared spectra obtained
and interpreted. Mass spectrometric investigation of borazole
and B-deuterated borazole lead to the conclusion that a

hydrogen atom is abstracted preferentially from boron atoms in the mass spectrometer to give the $B_3N_3H_5^+$ fragment.

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