AN ABSTRACT OF THE THESIS OF

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    (Name)   (Degree)   (Major)

Chemistry

Date thesis is presented August 29, 1963

Title   Synthesis of the boron-boron bond

Abstract approved �_____
                            (Major professor)

A preparative method for potassium di-n-butylborate(I) in triethylamine solvent has been developed that is superior to the preparation previously reported in the literature. The reaction of Bu_2BK (Bu = n-butyl group) with halide-containing substances such as Bu_2BCl and BF_3 produces diboron compounds. The compounds are probably Bu_2BBBu_2 and Bu_2BBF_2 respectively. These compounds were not isolated but were characterized by their reactions with ethylene and by basic hydrolysis. Attempts to replace the n-butyl groups of the diboron compounds with fluoride from BF_3 resulted in their partial replacement, as evidenced by the formation of $BuBF_2$, but did not give uncomplexed B_2F_4.

In addition, the vapor pressure equation, infrared spectrum, heat of vaporization and Trouton's Constant were determined for n-butylborondifluoride, $BuBF_2$.

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Date thesis is presented ___August 29, 1963___

Typed by Penny A. Self

SYNTHESIS OF THE BORON-BORON
BOND

by

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A THESIS

submitted to

OREGON STATE UNIVERSITY

in partial fulfillment of
the requirements for the
degree of

MASTER OF SCIENCE

June 1964

ACKNOWLEDGEMENT

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SYNTHESIS OF THE BORON-BORON BOND

INTRODUCTION

Development of the organic chemistry of boron has occurred almost exclusively in the period since 1950. The organoboranes $(CH_3)_3B$ and $(CH_3CH_2)_3B$ were prepared some 100 years ago by Frankland (16) but little additional work was done until 1920. The pioneering work of such scientists as Alfred Stock and E. Krause in Germany and H. I. Schlesinger in the United States in the period 1920-1940 led to the preparation and characterization of other tri-alkylboranes, alkyldiboranes and metal tetraalkylborates, MBR_4. More recently, the development of the hydroboration reaction by Brown and co-workers (10) has led to a rapid increase in knowledge of the organic chemistry of boron since the process is of interest to both organic and inorganic chemists.

A second recent development that has not received an equiv-alent amount of attention has been the discovery that several mole-cules containing a boron-boron bond add symmetrically across a carbon-carbon double bond (15, 33) much as do the halogens.

$$\diagdown B-B\diagup \; + \; \diagup C=C\diagdown \longrightarrow \diagdown B-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-B\diagup$$
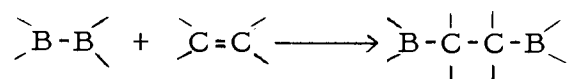
Interest in this process has been limited by the difficulties encoun-tered in synthesizing diboron compounds. The addition reaction of diboron compounds to olefins is potentially as useful as the hydro-boration process in the development of the organic chemistry of

boron. Applications to the chemistry of the higher hydrides of boron
is also likely since these latter substances presumably include
framework boron-boron bonds in their structures. It is, therefore,
deemed important that convenient syntheses of diboron compounds
be developed.

Stock (30) in the early 1920's first prepared B_2Cl_4 by
striking an arc between zinc electrodes immersed in liquid BCl_3.
This method was later improved by Schlesinger and his co-workers
(32, 34) by the use of a glow discharge through gaseous BCl_3 using
mercury electrodes. The development of an elaborate cycling
system for the BCl_3 allowed the production of about eight grams of
B_2Cl_4 per week. Hg_2Cl_2 is formed in the oxidation half-reaction.
Holliday and Massey (20) further refined the discharge and system
to produce yields of about 0.1 g per hour. Recently microwave
discharge has been used to prepare B_2Cl_4 (17). By this method
microwave excitation of gaseous BCl_3 produces B_2Cl_4 and Cl_2. Di-
boron tetrabromide and diboron tetraiodide were prepared by
Schlesinger and co-workers (32) by treating B_2Cl_4 with the appro-
priate boron trihalide and removing the more volatile BCl_3 as it
formed in the halogen exchange reaction. Diboron tetrabromide was
also prepared by passing an argon-boron tribromide mixture through
a discharge between nickel or mercury electrodes (24). B_2I_4 and
some other lower iodides of boron have been prepared from gaseous
BI_3 by the use of radio-frequency electrodeless discharge at room
temperature (28). Finch and Schlesinger (15) also prepared B_2F_4

by successive treatments of B_2Cl_4 with SbF_3.

Chemical reduction of trimeric boron compounds has also been used for the preparation of diboron compounds. Heller and Polanyi (18) treated sodium vapor with BBr_3 and BCl_3 in a study of reaction velocities but made no attempt to isolate reaction products. Down and co-workers (13) used sodium-potassium alloy to reduce BCl_3 to lower chlorides in an ethylene glycol-dimethyl ether solvent but did not isolate products. Fedorov et al.(14) reduced BCl_3 to boron using zinc vapor at $1000^{\circ}C$. No intermediate reduction products were obtained.

Wiberg (36) reported the preparation of tetraalkoxydiborons, $B_2(OR)_4$, by reduction of chlorodialkoxyboranes with sodium amalgam but attempts to repeat this preparation have not been successful. Recently, Brotherton and co-workers (6) have succeeded in preparing several of the tetraalkoxydiborons by the low temperature addition of the alcohol and four equivalents of hydrogen chloride to tetrakis-(dimethylamino)-diboron in diethyl ether solution.

$$(Me_2N)_4B_2 + 4\,ROH + 4\,HCl \longrightarrow (RO)_4B_2 + 4\,Me_2NH_2Cl$$
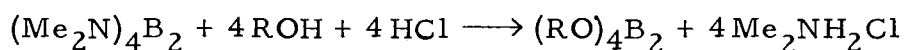
Tetrakis-(dimethylamino)-diboron is prepared by the reaction of highly dispersed molten sodium with either chloro- or bromo-bis-(dimethylamino)-borane (7).

$$2\,(Me_2N)_2BX + 2\,Na \longrightarrow (Me_2N)_4B_2 + 2\,NaX$$

The acid hydrolysis of tetrakis-(dimethylamino)-diboron yields tetrahydroxydiboron which may be dehydrated to boron monoxide (22).

$$(Me_2N)_4B_2 + 4H_2O + 4HCl \longrightarrow B_2(OH)_4 + 4Me_2NH_2Cl$$

$$B_2(OH)_4 \xrightarrow[\Delta]{} B_2O_2 + 2H_2O$$
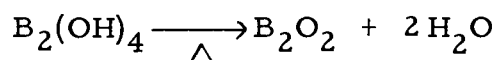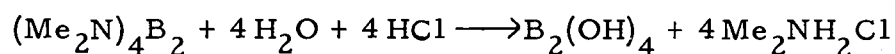
The boron monoxide has been used to prepare B_2Cl_4 (22) and B_2F_4 (8).

Boron monoxide was initially prepared from magnesium boride, Mg_3B_2, by several different methods which varied only in the manner of hydrolysis of the boride (25, 26). In the method initially used by Ray (25), the solution after extraction of the boride with water was treated with alkali to precipitate the salt, $Na_2H_2B_2O_4$. This salt was then acidified and dehydrated to form the monoxide. Ray and Shina (26) treated the boride extraction solution with concentrated ammonia to form the ammonium salt, $(NH_4)_2B_2O_2(OH)_2$, which was then heated in vacuo to form B_2O_2.

Auten and Kraus (1) reported the reduction of di-n-butylboron chloride by means of sodium-potassium alloy in diethyl ether solution. They also reported some reactions of the resulting compound that were of use in its characterization.

With one equivalent of metal, the free group Bu_2B (Bu = n-butyl group) or its polymer is formed.

$$Bu_2BCl + K \longrightarrow Bu_2B + KCl$$
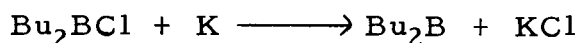
Attempts to separate the so-called "dibutylboron", Bu_2B, from the solvent by distillation in vacuo resulted in disproportionation of the product to form tri-n-butylboron and a solid, presumably monobutylboron.

$$2 (Bu_2B) \longrightarrow Bu_3B + BuB$$
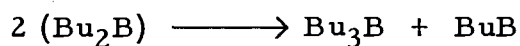
Bu_2B was not characterized other than by establishing the absence of alkali metal ion in its formulation and by isolation of Bu_3B from the above reaction.

When two equivalents of alkali metal are used, the di-n-butylboron chloride is reduced to potassium di-n-butylborate(I).

$$Bu_2BCl + 2 K(Na) \longrightarrow Bu_2BK + KCl + 2 Na$$
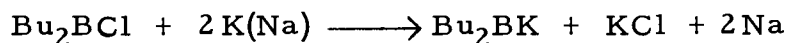
The nature of Bu_2BK was established by its reactions with methyl iodide to form methyl di-n-butylborane and with excess hydrogen chloride to form hydrogen, di-n-butylboron chloride and potassium chloride.

$$Bu_2BK + CH_3I \longrightarrow Bu_2BCH_3 + KI$$

$$Bu_2BK + 2 HCl \longrightarrow Bu_2BCl + H_2 + KCl$$
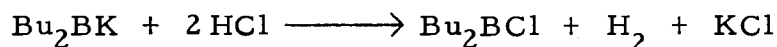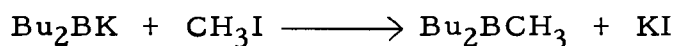
Upon treatment of Bu_2BK with one mole of hydrogen chloride per mole of Bu_2BK, the final products are tri-n-butylboron, a non-volatile product and hydrogen. Similar results were realized by treatment of Bu_2BK with triethylammonium chloride.

$$2\,Bu_2BK + 2\,HCl \longrightarrow Bu_3B + BuB + H_2 + 2\,KCl$$

$$2\,Bu_2BK + 2\,(C_2H_5)_3NHCl \longrightarrow Bu_3B + BuB + 2\,(C_2H_5)_3N +$$
$$H_2 + 2\,KCl$$
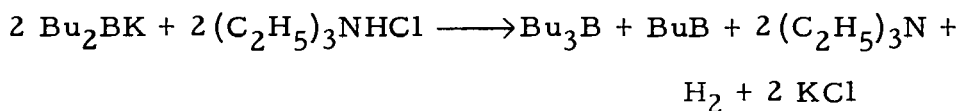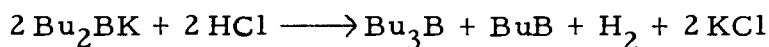
Attempts to isolate Bu_2BK were unsuccessful.

The objective of this research is to investigate the nature of the compound, potassium di-n-butylborate(I), first prepared by Auten and Kraus (1), with particular reference to its use as an intermediate in the preparation of organoboranes. This compound, presumably containing the di-n-butylborate(I) anion, is potentially useful for the synthesis of unsymmetrically-substituted boranes of the general formula Bu_2BX were X is any group capable of being covalently bonded to boron. It should also serve as an intermediate in the synthesis of compounds containing a boron-boron bond and it is this potential use that will be of primary interest in this work.

If "dibutylboron" is in fact the dimer, tetra-n-butyldiboron, the molecule contains a boron-to-boron bond. The unsuccessful attempt to isolate the compound by distillation may then be partly attributed to its high molecular weight. It should also be noted that association with the nucleophilic solvent diethyl ether to form a complex would further reduce the possibility of distillation without decomposition.

Three areas of investigation are suggested. An alternative solvent for the preparation of Bu_2BK and "Bu_2B" will be sought, a solvent that will allow easier separation of the desired compounds.

The solvent must be unreactive toward sodium-potassium alloy (and therefore aprotic), it must be volatile enough to allow ready transport by vacuum distillation at room temperature, it must be polar enough to dissolve the potassium di-n-butylborate(I), and it must be possible to easily destroy any complex formed with the product. Triethylamine appears to fulfill these requirements. Its complexes with many boron-containing compounds can be destroyed by treatment with anhydrous HCl at room temperature.

$$(CH_3CH_2)_3NBX_3 + HCl \longrightarrow (CH_3CH_2)_3NHCl + BX_3$$
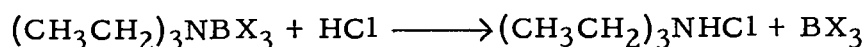
Attempts will be made to replace the bulky n-butyl groups of the presumed tetra-n-butyldiboron with smaller groups thus producing a more volatile diboron compound. Fluoride substituents appear promising since the compound B_2F_4 is known to be quite stable toward decomposition to BF_3 and polymers (8, 15).

The third area of investigation is the characterization of the presumed diboron compound without its prior isolation. Two generally accepted tests for diboron compounds are the production of hydrogen gas by basic hydrolysis (6, 7, 15, 28, 34) and the addition of diboron compounds across the carbon-carbon double bonds of simple olefins (15, 33). The general equation for the basic hydrolysis is

$$2\ OH^- + {>}B\text{-}B{<} \longrightarrow 2\ {>}BO^- + H_2.$$
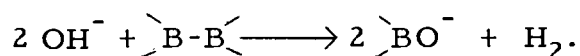
One mole of hydrogen is produced per mole of boron-boron bond.

Unreacted alkali metal, substances containing B-H bonds, and other substances that produce hydrogen gas under these conditions must be absent. Diboron compounds add to olefins, such as ethylene, by the general reaction

$$\diagup\hspace{-0.3em}B-B\hspace{-0.3em}\diagdown \;+\;\; CH_2\!=\!CH_2 \longrightarrow \diagup\hspace{-0.3em}BCH_2CH_2B\hspace{-0.3em}\diagdown\;.$$
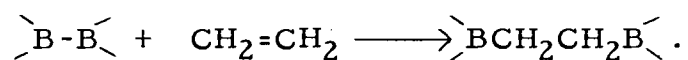
The uptake of ethylene serves as an indication of the presence of a diboron compound and under favorable circumstances as a quantitative measure of boron-boron bond content.

EXPERIMENTAL

Apparatus and Equipment

Unless otherwise noted all of the experiments were performed using standard vacuum apparatus and technique as described by Sanderson (27). On several occasions, special glass reaction vessels were constructed and are described in experiments where they were used.

Determination of Reagent Purity

The most convenient means for the determination of reagent purity in a vacuum line is the measurement of one or more vapor pressures at specific temperatures and comparison of these pressures with published values. When it was convenient to measure a vapor pressure greater than 100 mm Hg, agreement within one percent of the literature value was considered a sufficient criterion for purity. When, because of lower volatility, it was not convenient to measure vapor pressure of this magnitude additional proof of purity was obtained as follows. Approximately half of a sample was distilled away and the vapor pressures of the distillate and residue were compared at a common temperature. Agreement within one percent was considered evidence of chemical purity. Alternatively, the vapor pressure of the sample was measured in vessels where the gas volume was varied 100 fold or more. Again, agreement within one percent under these conditions of wide variance of mole

fraction in the vapor state was considered evidence of purity.

The literature values for vapor pressures of common chemicals are from the International Critical Tables (35) or a compilation by Stull (31).

Reagents

Di-n-butylboron chloride

Di-n-butylboron chloride was prepared according to instructions of Booth and Kraus (5). The boiling point was 65-68°C at a pressure of 15-17 mm. This value agrees with the vapor pressure data reported by Skinner and Tees (29).

Triethylamine

Triethylamine was dried over calcium hydride, passed through a column containing P_2O_5 supported on glass beads, passed through a -30°C trap and condensed at -80°C. The vapor pressure was 18.5 mm at 0°C; the accepted value is 18.3 mm. The treatment with P_2O_5 removes any traces of primary and secondary amines which are present and which would react with the alkali metal (2, p. 14, 17).

Ethylene

Tank ethylene from Ohio Chemical and Surgical was fractionated through -160°C into a -196°C trap. The vapor pressure at

-112°C was 455 mm; accepted 455 mm.

Sodium-potassium alloy

Commercially available sodium and potassium were mixed to form the liquid alloy as described by Birmingham (4).

Nitrogen

When nitrogen was used as an inert atmosphere, it was purified by passage through a heated column of copper turnings and subsequent passage through a column of $CaCl_2$, BaO and P_2O_5 packed on glass beads. In several instances prepurified nitrogen supplied by Matheson (99.99 + percent nitrogen) was used and then it was passed only through the drying tube of $CaCl_2$, BaO and P_2O_5.

Boron trifluoride and hydrogen chloride

These compounds were obtained as compressed tank gases from the Matheson Company and each was purified by fractional condensation until the vapor pressure agreed with the literature value. For BF_3 the vapor pressure was 289 mm at -112°C (accepted 291 mm) and for HCl it was 126 mm at -112°C (accepted 127 mm).

Preparations and Reactions

Preparation of potassium di-n-butylborate(I)

Potassium di-n-butylborate(I) was prepared by the method

described by Auten and Kraus (1) with certain modifications.

Fragile bulbs containing 2.5 to 3.0 g of Bu_2BCl were sealed into

the reaction apparatus (at point E) shown in Figure I. The apparatus

was sealed to the vacuum line at A and evacuated while outlet B was

closed with a thin glass seal. Nitrogen was admitted through A

until a pressure higher than atmospheric pressure was reached.

The nitrogen flow was continued while the seal at B was opened and

five ml of liquid sodium-potassium alloy was introduced by use of a

hypodermic needle. The opening at B was then sealed using the

constriction provided. The apparatus was re-evacuated and about

ten ml of triethylamine condensed in. The constriction at A was

sealed and the apparatus, with the reactants at $-80^\circ C$, was shaken

to break the fragile bulbs.

Almost immediately upon warming a white solid was formed

and some heat produced. The white solid was later examined and

gave a positive test for chloride ion. The temperature of the reac-

tants was allowed to slowly attain room temperature. The brown

color characteristic of the product Bu_2BK developed upon standing

overnight. After several days the solution was filtered through a

medium porosity fritted glass filter, F in Figure I, into the storage

bulb D. Triethylamine was alternately condensed back into E and

Figure I. Reaction Vessel
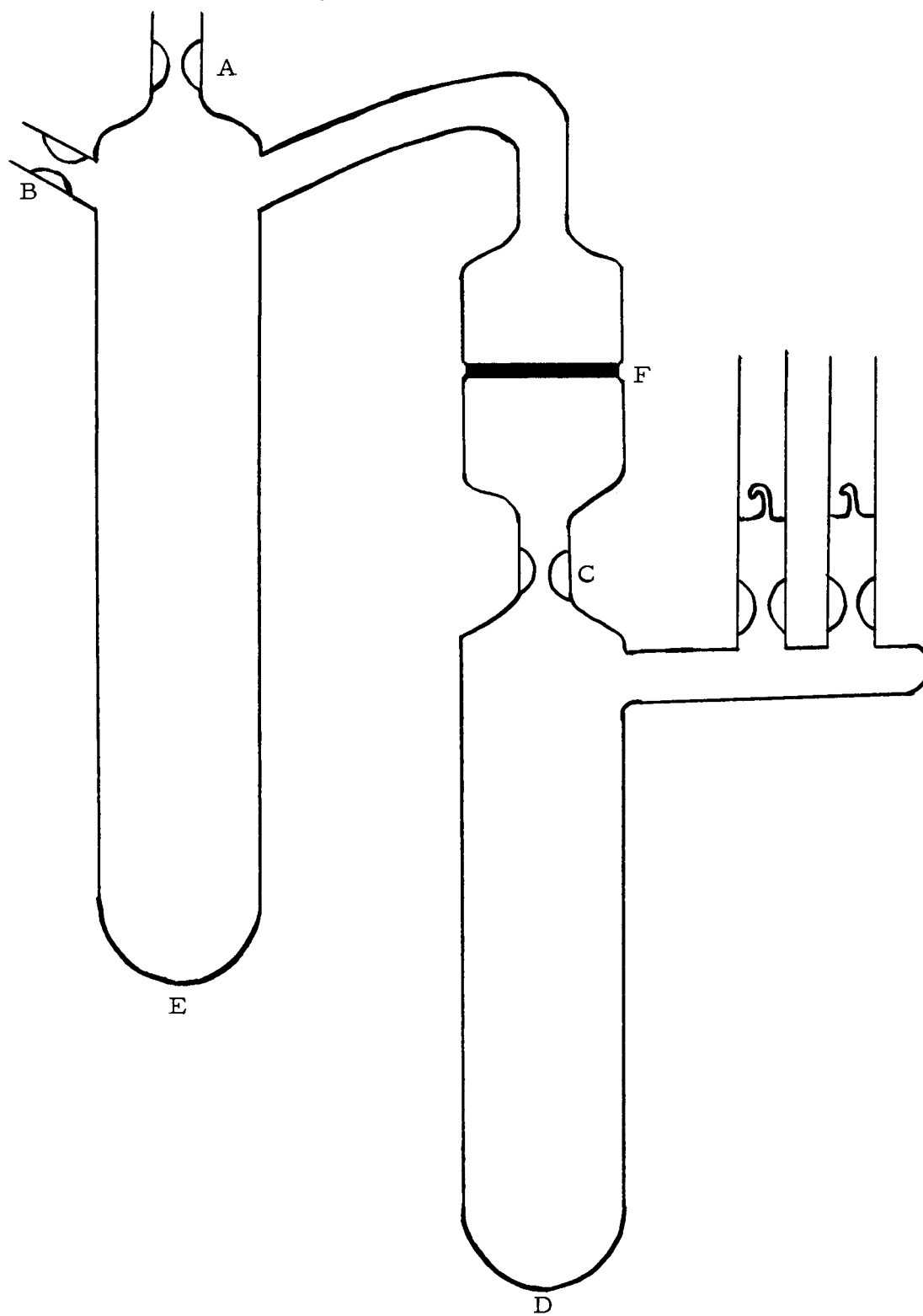
filtered into D until it showed no trace of color. The apparatus was then sealed at the constriction C and the product was stored for later use. The yield, determined by a gravimetric chloride analysis of the water soluble solid residue, is about 70 percent based on the original amount of Bu_2BCl. In all other preparations of Bu_2BK, it was assumed that the yield was the same.

$$Bu_2BCl + 2K(Na) \longrightarrow Bu_2BK + KCl + 2Na$$
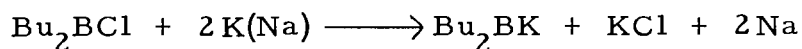
Preparation of tetra-n-butyldiboron

Fragile bulbs containing about 1.6 g (ten mmoles) of Bu_2BCl were sealed into an apparatus very similar to the one shown in Figure I. It was so arranged that the Bu_2BK solution previously prepared could be poured into the tube containing the fragile bulbs. The original tube containing the Bu_2BK was then sealed off and removed and the bulbs of Bu_2BCl were broken. The reaction was rapid at $-80^{o}C$ and produced a white solid which later tested positive for chloride. After the initial reaction had ceased, the temperature of the mixture was allowed to slowly attain room temperature. On standing for six to ten hours the color of the solution turned from dark brown to light yellow. The solution was filtered through a medium porosity fritted glass filter and the solid washed several times with triethylamine.

$$Bu_2BK + Bu_2BCl \longrightarrow Bu_2BBBu_2 + KCl$$
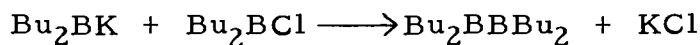
The water soluble solid was found to contain 5.5 mmoles of chloride determined as AgCl. This result indicated about a 55 percent yield based on consumption of Bu_2BCl.

Reaction of tetra-n-butyldiboron with ethylene

A solution of Bu_4B_2, containing approximately 7.5 mmoles and prepared in the above fashion, was treated with 11.22 mmoles of ethylene for five days. The volatile fraction was separated by fractional condensation from $0^\circ C$ through $-80^\circ C$ into a $-196^\circ C$ trap. The $-80^\circ C$ fraction was triethylamine and the $-196^\circ C$ fraction was ethylene. The ethylene was returned to the reaction flask and allowed to stand at room temperature for an additional 18 hours. The mixture was then fractionated through $-80^\circ C$, $-160^\circ C$ and $-196^\circ C$ traps. The $-196^\circ C$ fraction contained 8.58 mmoles of pure ethylene as determined by vapor pressure. A total amount of 2.64 mmoles of ethylene had reacted.

$$Bu_2BBBu_2 \; + \; C_2H_4 \longrightarrow Bu_2BC_2H_4BBu_2$$
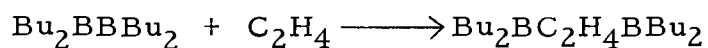
Basic hydrolysis of tetra-n-butyldiboron

A sample containing about 2.7 mmoles of Bu_4B_2 solution (prepared from about 5.5 mmoles of Bu_2BK) was hydrolyzed by slowly adding five ml of two molar NaOH to the solution. After standing at room temperature overnight, the triethylamine layer was colorless and there was no more visible reaction. A total of

3.45 mmoles of non-condensable gas was present.

$$Bu_2BBBu_2 + 2\,NaOH \longrightarrow 2\,Bu_2BONa + H_2$$
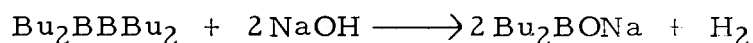
Reaction of tetra-n-butyldiboron with boron trifluoride

An attempt was made to replace the butyl groups of Bu_4B_2 with fluoride ions by treatment with boron trifluoride. Uncomplexed triethylamine was removed from the sample insofar as possible and excess BF_3 added. After allowing the mixture to stand for several days it was fractionated through $-30^{\circ}C$, $-112^{\circ}C$ and $-196^{\circ}C$ traps. The $-196^{\circ}C$ fraction contained BF_3 identified by its vapor pressure (290 mm at $-112^{\circ}C$; accepted 291 mm) and the $-112^{\circ}C$ fraction was a complex mixture. One component of the mixture was isolated and identified as $BuBF_2$ (see details on page 19). No other components could be identified and in particular, B_2F_4 was not among the products. Excess anhydrous HCl was added to the $-30^{\circ}C$ fraction and the non-volatile material in the reaction flask. A reaction occurred upon warming from $-80^{\circ}C$ to room temperature. Some non-condensable gas was formed during the reaction and 3.9 mmoles of HCl reacted. The material was then fractionated through $0^{\circ}C$, $-80^{\circ}C$, $-112^{\circ}C$ and $-196^{\circ}C$. A fraction condensed in each trap. Since the vapor pressure of the desired B_2F_4 (15) indicated that it should condense at $-112^{\circ}C$, the $0^{\circ}C$ and $-80^{\circ}C$ fractions were not investigated. The $-196^{\circ}C$ fraction contained the unreacted HCl with a small amount of BF_3 (v.p. 139 mm at $-112^{\circ}C$; accepted 126 mm for HCl

and 291 mm for BF_3 at $-112^{\circ}C$). The $-112^{\circ}C$ fraction was identified as pure $BuBF_2$.

Reaction of potassium di-n-butylborate(I) with boron trifluoride

A sample containing about 12 mmoles of Bu_2BK was sealed to the vacuum line and excess triethylamine was condensed away into a $-80^{\circ}C$ trap. A thick syrupy liquid that was dark brown in color remained. To this was added excess BF_3. No reaction occurred at $-80^{\circ}C$ but a slow reaction was apparent at $0^{\circ}C$. The brown color lightened to a pale amber and a white solid formed.

$$Bu_2BK + BF_3 \longrightarrow Bu_2BBF_2 + KF$$
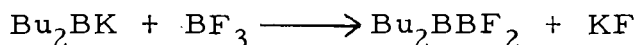
After standing several days the excess BF_3 was condensed away and anhydrous HCl added to the remaining components. A reaction occurred producing non-condensable gas. The number of moles of non-condensable gas was about one-half of the amount of HCl that reacted. In a typical reaction about 7.5 mmoles of non-condensable was produced and 14.25 mmoles of HCl reacted.

$$Bu_2BK + 2HCl \longrightarrow Bu_2BCl + KCl + H_2$$
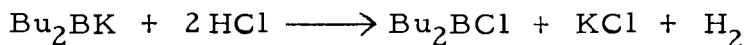
On fractionation through $-127^{\circ}C$ into $-196^{\circ}C$ unreacted HCl was recovered but no BF_3. It thus appears that HCl will not displace BF_3 from the amine complex and that the reaction of Bu_2BK with BF_3 is about 50 percent complete.

The -127°C fraction was returned to the reaction vessel and BF$_3$ was again added in excess. After standing several more days the reaction mixture was fractionated through -80°C, -127°C and -196°C. The -196°C fraction contained pure BF$_3$. A total amount of 35 mmoles of BF$_3$ was used in the reaction. The -127°C fraction was a pure compound identified by vapor pressure and molecular weight as BuBF$_2$. (105 g/mole experimental; 105.8 g/mole calculated.) The -80°C fraction was passed through -45°C, -63°C, -80°C and -196°C. The -45°C trap contained a slightly volatile liquid but it was not investigated since the desired B$_2$F$_4$ would not condense at this temperature. Nothing condensed at -63°C and only a trace at -196°C. The -80°C fraction was more BuBF$_2$.

Reaction of di-n-butyldifluorodiboron with ethylene and with aqueous base

A sample containing about eight mmoles of Bu$_2$BK was split visually into two equal volumes. The excess triethylamine was distilled off and excess BF$_3$ was added to each. After allowing it to stand for 24 hours, the excess BF$_3$ was removed by fractionating through -80°C, -127°C and -196°C. The -196°C fraction contained pure BF$_3$. The -80°C and -127°C fractions were returned to the reaction tubes.

To one reaction tube was added 5.77 mmoles of ethylene. This was allowed to stand for 24 hours at room temperature and then fractionated through -80°C, -127°C and -196°C. The -196°C fraction

contained 3.74 mmoles of ethylene (v.p. 139 mm at -127°C;

accepted 139 mm). A total of 2.03 mmoles of ethylene had reacted.

To the second reaction tube was added five ml of two molar

sodium hydroxide. After mixing the base with the sample and

allowing the reaction to proceed at room temperature, 3.26 mmoles

of non-condensable gas were formed. The non-condensable would

be produced from both the Bu_2BK and Bu_2BBF_2.

The physical properties and infrared spectrum of n-butylborondifluoride

The compound identified as n-butylborondifluoride, $BuBF_2$,

was characterized by a number of properties. The increase in

weight of an evacuated weighing bulb resulting from the addition of

0.365 mmoles of material was 38.2 mg. The experimental mole-

cular weight is therefore 104.6. The calculated molecular weight

for $C_4H_9BF_2$ is 105.8. Vapor pressure data is listed in Table I.

The calculated data were obtained from the equation $\log_{10} P_{mm} =$

$7.935 - \dfrac{1558}{T}$.

Table I. Vapor Pressure of n-butylborondifluoride

Temperature °C	-47	-30.7	-23	0	12	17	22
v.p. mm (obs)	9	34	52	169	296	363	447
v.p. mm (calc)	10.7	32	50.2	170	295	363	447

The curve was extrapolated to give a normal boiling point of $36^{\circ}C$. The calculated normal boiling point from the vapor pressure equation is $35.5^{\circ}C$. Buls reports a normal boiling point of $35^{\circ}C$ (11) and McKusker gives a value of $36.3-36.5^{\circ}C$ at 742 mm (23) but neither reports vapor pressure data. The heat of vaporization and Trouton's Constant are 7130 calories per mole and 23.1 respectively.

The infrared spectrum was determined from 650 to 4000 wave numbers using a 100 mm gas cell and sodium chloride windows. A Beckman Model IR-7 spectrophotometer was used for the determination. The spectrum for $BuBF_2$ is shown in Figure II. The initial sample was refractionated through $-80^{\circ}C$, $-95^{\circ}C$ and $-196^{\circ}C$. The $-95^{\circ}C$ fraction was used for the spectrum determination.

It is also interesting to note that $BuBF_2$ is quite soluble in mercury and this presented some problems in storage of the compound in the vacuum line.

Figure II. Infrared spectrum of n-butylborondifluoride

Percent Transmission

Wave Number x 10^2

a   30 mm Hg
b   10 mm Hg
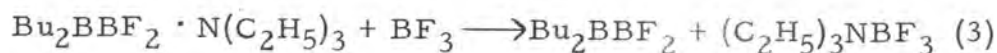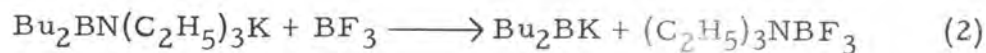c   4 mm Hg
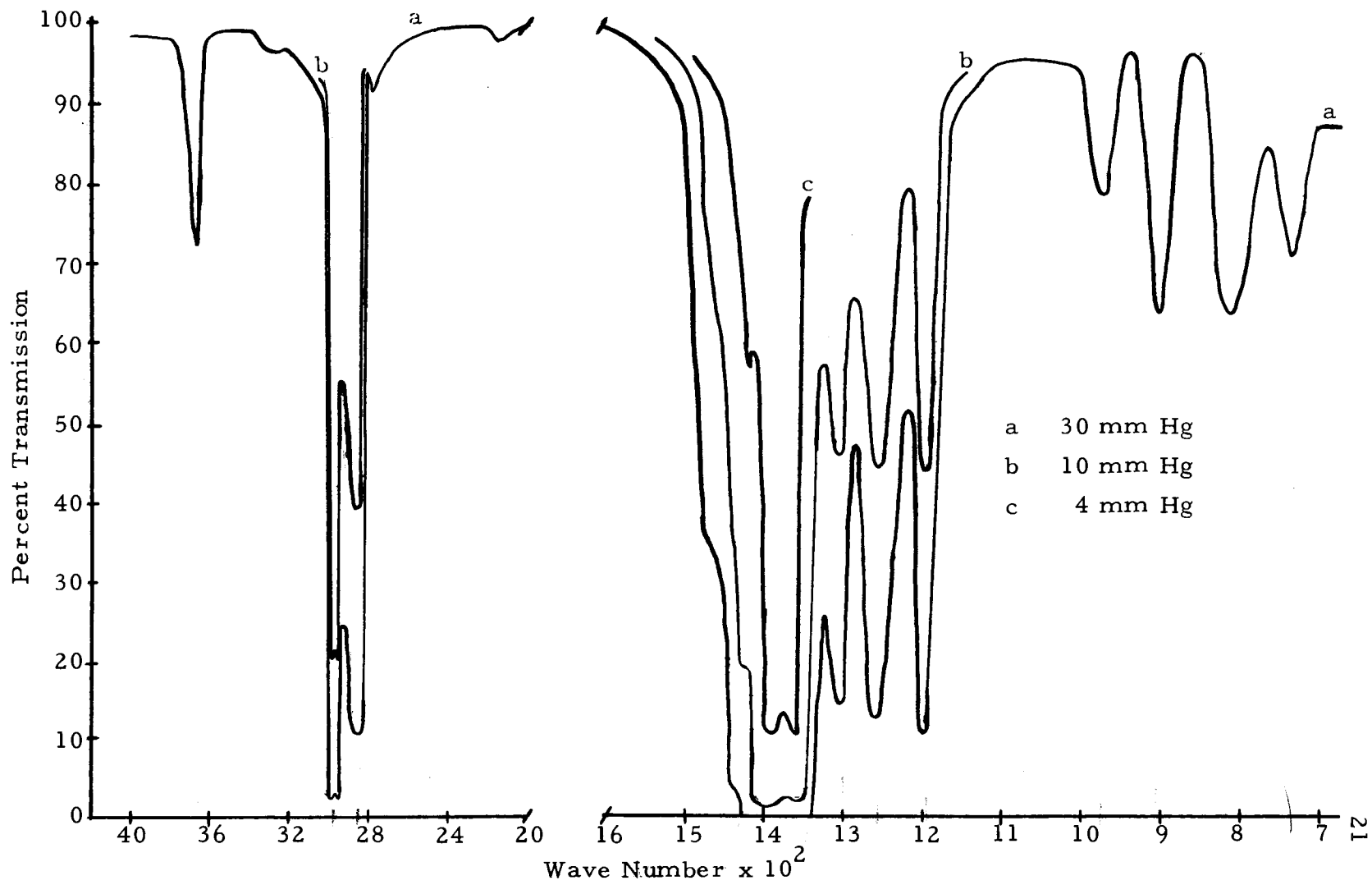
DISCUSSION OF RESULTS

Potassium di-n-butylborate(I) can be used as an intermediate in the preparation of organoborane compounds of the type Bu_2BX where X is any group capable of being covalently bonded to boron and thus in the formation of diboron compounds. The so-called "dibutylboron", Bu_2B, of Auten and Kraus (op. cit.) formed by the reaction of Bu_2BK and Bu_2BCl apparently is the dimer, Bu_2BBBu_2, containing a boron-boron bond. The compound was not isolated but was characterized by the reaction with ethylene and by basic hydrolysis.

Potassium di-n-butylborate(I) also reacts readily with BF_3 to form the probable compound Bu_2BBF_2. Again this compound was not isolated but its existence was confirmed by basic hydrolysis and by its reaction with ethylene.

Triethylamine was superior to diethyl ether as a solvent for the preparation of Bu_2BK. The reaction time was considerably shorter (24 hours as compared to at least 48 hours) and the yield of Bu_2BK was better (70 percent as compared to 60 percent obtained by Auten and Kraus). The reaction between the potassium di-n-butyl-borate(I)-triethylamine complex and boron trifluoride involves both the formation of a diboron compound plus potassium fluoride and the formation of boron trifluoride-triethylamine complex.

$$Bu_2BN(C_2H_5)_3K + BF_3 \longrightarrow Bu_2BBF_2 \cdot N(C_2H_5)_3 + KF \quad (1)$$
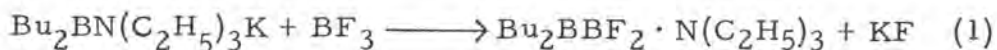
The boron trifluoride-triethylamine complex is formed from occluded triethylamine solvent and may also arise by displacement of Bu_2BK or Bu_2BBF_2.

$$Bu_2BN(C_2H_5)_3K + BF_3 \longrightarrow Bu_2BK + (C_2H_5)_3NBF_3 \qquad (2)$$

$$Bu_2BBF_2 \cdot N(C_2H_5)_3 + BF_3 \longrightarrow Bu_2BBF_2 + (C_2H_5)_3NBF_3 \quad (3)$$
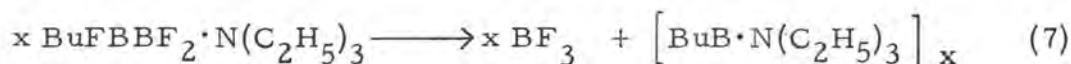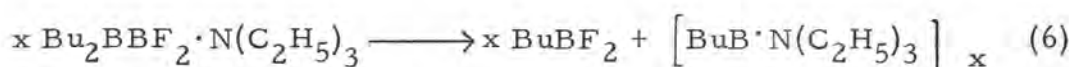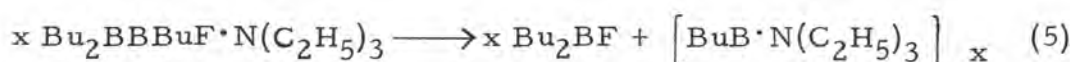
Reaction (2) is not likely to occur since the brown color of the potassium salt was discharged at low temperature upon addition of BF_3. Thus reaction (1) appears to occur quite readily. Little is known about the Lewis acidity of diboron compounds as compared to the boron trihalides. Unpublished work of John Hansen of this laboratory shows B_2F_4 to be a stronger Lewis acid than BF_3. Tri-alkylboranes are weaker Lewis acids than the boron trihalides so then, by analogy, n-butyl-substituted diboron compounds should be weaker Lewis acids than B_2F_4. Whether they are weaker acids than BF_3 is unknown. Thus, reaction (3) may or may not take place.

Attempts to produce B_2F_4 by displacement of all the n-butyl groups of Bu_2BBBu_2 and Bu_2BBF_2 with fluorides were unsuccessful. Some exchange must occur since $BuBF_2$ was isolated as a product from treatment of both of these compounds with BF_3. These results suggest that the compound $BuFBBF_2$ is formed.

$$Bu_2BBF_2 \cdot N(C_2H_5)_3 + BF_3 \longrightarrow BuFBBF_2 \cdot N(C_2H_5)_3 + BuBF_2$$

$$(4)$$
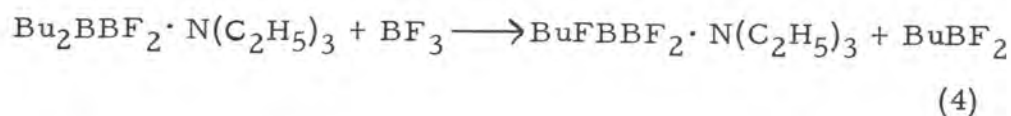
It is possible that the last n-butyl group is also displaced from the diboron compound by fluoride and that $B_2F_4 \cdot N(C_2H_5)_3$ thus produced can not be isolated as a volatile compound either by distillation in vacuo at room temperature or by displacement of the amine by BF_3.

One other possibility should be mentioned. The unsymmetrically-substituted diboron compounds may disproportionate to give polymeric materials containing boron-boron bonds. Some examples are:

$$x \, Bu_2BBBuF \cdot N(C_2H_5)_3 \longrightarrow x \, Bu_2BF + \left[BuB \cdot N(C_2H_5)_3 \right]_x \quad (5)$$

$$x \, Bu_2BBF_2 \cdot N(C_2H_5)_3 \longrightarrow x \, BuBF_2 + \left[BuB \cdot N(C_2H_5)_3 \right]_x \quad (6)$$

$$x \, BuFBBF_2 \cdot N(C_2H_5)_3 \longrightarrow x \, BF_3 + \left[BuB \cdot N(C_2H_5)_3 \right]_x \quad (7)$$

$BuBF_2$ was never formed from $Bu_2BBF_2 \cdot N(C_2H_5)_3$ except upon treatment with excess BF_3 for long periods of time. BF_3 may serve as a catalyst for the disproportionation reaction (6) but the exchange reaction (4) would be a more reasonable hypothesis for $BuBF_2$ formation since BF_3 was consumed as $BuBF_2$ was formed. The same argument applies to reaction (5). After long treatment of $Bu_2BBF_2 \cdot N(C_2H_5)_3$ with excess BF_3 followed by removal of BF_3 and $BuBF_2$, the non-volatile residue gave off small additional amounts of BF_3 upon standing in vacuo. This additional BF_3 may have been produced by reaction (7) or may have simply been a result of slow release of BF_3 from the viscous mixture when BF_3 pressure was decreased.

Because n-butylborondifluoride consistently appeared in the experiments and a normal boiling point of $35^{\circ}C$ reported by Buls (op. cit.) and a value of $36.3-36.5^{\circ}C$ reported by McKusker (op. cit.) were the only published data, further characterization of the compound was carried out. The compound was identified by vapor pressure data, molecular weight determinations and by the infrared spectrum. Vapor pressure data were found to conform to the equation $\log_{10} P_{mm} = 7.935 - \dfrac{1558}{T}$ and the experimental molecular weight was determined to be 104.6. The calculated molecular weight for $C_4H_9BF_2$ is 105.8. The heat of vaporization and Trouton's Constant are 7130 calories per mole and 23.1 respectively. The infrared spectrum of $BuBF_2$ as shown in Figure II is in good agreement with the spectrum of methylborondifluoride reported by Becher (3).

The results of this work suggest that the less volatile fraction produced from the reaction between Bu_2BK and excess BF_3 be examined further. This fraction may contain Bu_2BF, Bu_2BBF_2 and $B_2F_4 \cdot N(C_2H_5)_3$. Separation of such a mixture is not feasible by fractional condensation methods in a vacuum line both because of the low volatility of the materials and the low separation efficiency of the method. High temperature gas chromatography would appear to be a more efficacious method.

The preparative route to diboron compounds, developed by Brotherton and co-workers (6, 7) after this work was initiated, appears to offer a more useful means of obtaining these substances

for use as synthetic intermediates. The method developed in this laboratory for the preparation of potassium di-n-butylborate(I) has been applied satisfactorily when this compound was used as an intermediate in the preparation of other unsymmetrically substituted boranes.

SUMMARY

A preparative method for potassium di-n-butylborate(I) in triethylamine solvent has been developed that is superior to the preparation previously reported by Auten and Kraus (1). The reaction of this compound with halide-containing substances such as Bu_2BCl and BF_3 produces diboron compounds. Attempts to replace n-butyl groups of diboron compounds with fluoride from BF_3 resulted in their partial replacement as evidenced by the formation of $BuBF_2$ but did not give uncomplexed B_2F_4.

The compound $BuBF_2$ was partially characterized.

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