The Preparation of Some Typical Organoboron Compounds

Glen David Barbaras

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THE PREPARATION
OF SOME TYPICAL
ORGANOBORON COMPOUNDS

By
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A Thesis Submitted to the Faculty of the
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of Bachelor of Science

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# TABLE OF CONTENTS

I. List of Illustrations  
   Page  

II. Preface  
   Page iii

III. Introduction  
   The Work Done by Other Investigators  
   Page 1  

   Organoboron Compounds in the Interpretation of Modern Electronic Theories of Organic Reactions  
   Page 8

   Statement of the Problem  
   Page 15

IV. Experimental Methods  
   The Preparation of Anhydrous Ether  
   Page 18

   The Preparation of n-Butyl Bromide  
   Page 19

   The Preparation of the Grignard Reagent, n-Butyl Magnesium Bromide  
   Page 20

   The Preparation of Boron Trifluoride Etherate  
   Page 22

   The Preparation of Tri-n-butyl Borine  
   Page 23

   Apparatus  
   Page 23

   Procedure  
   Page 28

   The Vacuum Distillation of Tri-n-butyl Borine  
   Page 31

   Reactions of Tri-n-butyl Borine  
   Page 35

   The Preparation of Butane Boronic Acid  
   Page 40

   Apparatus  
   Page 40

   Procedure  
   Page 44

   Reactions of Butane Boronic Acid  
   Page 49

   The Preparation of Methyl Borate  
   Page 51

V. Discussion of Results and Conclusions  
   Page 58

VI. Annotated Bibliography  
   Page 63
## LIST OF ILLUSTRATIONS

<table>
<thead>
<tr>
<th>PLATE</th>
<th>Description</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.</td>
<td>Photograph of the Apparatus for the Preparation of Tri-n-butyl Borine.</td>
<td>26</td>
</tr>
<tr>
<td>II.</td>
<td>Drawing of the Apparatus for the Preparation of Tri-n-butyl Borine.</td>
<td>27</td>
</tr>
<tr>
<td>III.</td>
<td>Photograph of the Apparatus for the Vacuum Distillation of Tri-n-butyl Borine.</td>
<td>32</td>
</tr>
<tr>
<td>IV.</td>
<td>Drawing of the Apparatus for the Vacuum Distillation of Tri-n-butyl Borine.</td>
<td>33</td>
</tr>
<tr>
<td>V.</td>
<td>Photograph of the Apparatus for the Preparation of Butane Boronic Acid.</td>
<td>42</td>
</tr>
<tr>
<td>VI.</td>
<td>Drawing of the Apparatus for the Preparation of Butane Boronic Acid.</td>
<td>43</td>
</tr>
<tr>
<td>VII.</td>
<td>Drawing of the Apparatus for the Preparation of Methyl Borate.</td>
<td>54</td>
</tr>
</tbody>
</table>
PREFACE

Organoboron compounds have long been known, the first being prepared by Frankland as early as 1862. No particular interest in these compounds was aroused, however, because of the difficulty and expense of their preparation as well as their extreme instability. From time to time further attempts at their preparation were made and a few reactions were observed. With the rise of modern electronic theories of chemical combination, however, organoboron compounds were discovered to exhibit properties and undergo reactions which would substantiate these theories. Consequently, since 1936 possibly over a hundred of these compounds of many different types have been prepared. In November, 1939, in keeping with the rising interest in these compounds, Mr. Darwin Kaestner presented a paper before the graduate seminar of Marquette University, covering some of the developments in the field of organoboron compounds with emphasis on the organoboron acids. In the search for an interesting and unusual thesis the author was referred to this paper by Dr. Clifford R. Haymaker and wishes to thank him for the initial suggestion of this field of work. The author also wishes to express his sincere thanks to Dr. Herbert Heinrich, the director of this thesis, for his interest and valuable assistance in guiding the work, and to Mr. Arthur J. Haug for his thoughtful cooperation especially in the photographic work on the thesis.
INTRODUCTION

Perhaps the first successful attempt at preparing organoboron compounds was made by Frankland. He prepared tri-


methyl- and triethyl borine by the interaction of zinc alkyls and ethyl borate and observed that they are spontaneously inflammable in air. By the slow oxidation of triethyl borine \((\text{C}_2\text{H}_5)_3\text{B}\), he obtained the diethyl ester, \(\text{C}_2\text{H}_5\text{B}(\text{OC}_2\text{H}_5)_2\), which when hydrolyzed gave ethane boronic acid \(\text{C}_2\text{H}_5\text{B}(\text{OH})_2\). The theory that the controlled oxidation of trialkyl borines was a general method of preparation for the aliphatic boronic acids was substantiated by Krause and his co-workers who obtained the \(n\)-propyl, isobutyl, \(t\)-butyl,


and isoamyl compounds in this fashion. For the initial preparation of the trialkyl borines, Krause used neither the zinc alkyls nor mercury alkyls which had been used but employed boron trifluoride, \(\text{BF}_3\), and a Grignard reagent. During 1921, the same year in which Krause's results were first published, Stock and Zeidler reported their method for
the preparation of the trialkyl borines, which consisted of allowing gaseous boron trichloride, $\text{BCl}_3$, and the corresponding zinc alkyl to react without the presence of a solvent. Elaborate apparatus containing automatically opened expansion chambers and extreme cooling was necessary to prevent violent explosions. These investigators imagined that by undertaking a study of trimethyl and triethyl borine, they would be able to clear up the mechanism of the reactions of these compounds as well as the difficulties with valence and affinity, and then determine the molecular weights and size of the molecules. Most of these problems, however, are still far from being settled in 1941, twenty years later.

In order to prepare aliphatic or aromatic boronic acids directly, Michaelis and Becker\(^4\) had early used the organo-

\[\text{mercurials, and in 1909 Khotinski and Melamed}\(^5\) \text{found that both the aromatic and aliphatic boronic acids could be pre-}\]
pared readily by the action of Grignard reagents upon alkyl esters of boric acid. More recently Krause\(^6\) employed the

\[ \text{etherate of boron trifluoride instead of an alkyl borate.} \]

In 1938 Snyder, Kuch and Johnson\(^7\) found that the method of

\[ \text{Khotinsky and Melamed, with slight modifications, was the most convenient general procedure for the preparation of primary aliphatic boronic acids. They further reported obtaining good yields of tri-n-butyl borine\(^8\) by the action of Grignard reagents upon boron trifluoride, the method first successfully employed by Krause and Nitsche.} \]

An authoritative system of nomenclature for organoboron compounds has not yet been adopted. However, Dr. Austin M. Patterson\(^9\) has made suggestions for naming the three principal series of organoboron compounds. There are two main classes of alkyl boron acids. The first contains trivalent boron to which is attached directly an alkyl group and two
hydroxy groups, the formula being $RB(OH)_2$. These compounds are designated the alkane boronic acids, instead of "alkylboric acids" first suggested. If two OH groups of boric acid are considered as being replaced by alkyl radicals, an acid of the formula $R_2BOH$ is formed and is called a dialkyl borinic acid instead of "dialkyl boric acid". The product produced by substituting the same or different alkyl radicals for all of the OH groups of boric acid is termed a trialkyl borine, instead of "trialkyl boron" or "boron trialkyl" as used by the German and English chemists. All of these organoboron compounds are marked by the direct linkage of boron to carbon in contrast with the regular esters of boric acid in which an alkoxy group is attached to the boron and carbon is linked to boron through oxygen, i.e., $B(OR)_3$.

There is still another group of boron compounds which has come into considerable prominence within the last few years and that is the boron hydrides. Many organic derivatives of these compounds contain the direct boron to carbon linkage and have thus been properly called organoboron compounds. Theoretically, the simplest possible hydride has a formula similar to phosphine, $PH_3$, or arsine, $AsH_3$, and is similarly named borine, $BH_3$. The simplest hydride prepared, however, probably has the formula $B_2H_6$ and is called diborane. In a similar manner both $B_5H_9$ and $B_5H_{11}$ are called pentaboranes. The organic derivatives of the hydrides are named as derivatives of these basic compounds as soon as their
structures are ascertained.

The large amount of research carried out during the last thirty years on the hydrides of boron and their derivatives particularly by the German school associated with Alfred Stock and Egon Wiberg, has proved a source of fascination to many inorganic chemists. Some new reactions of great interest, discovered and studied by a group of American workers under H. I. Schlesinger and A. B. Burg at the University of Chicago have added substantially to the knowledge of this group of compounds. The following boron hydrides, which may be divided formally into two groups possessing the general formula \( B_nH_{n+4} \) and \( B_nH_{n+6} \) are described in the literature. 10

\[
\begin{align*}
B_nH_{n+4} & : \quad B_2H_6, B_5H_9, B_6H_{10}, B_{10}H_{14} \\
B_nH_{n+6} & : \quad B_4H_{10}, B_5H_{11}, B_6H_{12}
\end{align*}
\]


Stock and Zeidler 11 started out to study the reactions of trimethyl borine and triethyl borine but claimed that even though the basic formulas of these compounds would seem to indicate borine, BH3, as being the simplest hydride of boron, their experiments tended to show that "der ein-
The simplest of our displayed and probably about the simplest existent boronhydride is B2H6. Schlesinger and Burg, however, have reported evidence of

12


the transitory existence of borine, BH3. Organic derivatives other than the trialkyl or triaryl borines have also been prepared: e.g. borine carbonyl, BH3CO; borine trimethylamine and its methyl derivatives; the methyl triborine triamines. Additional complexes similar to those formed by

13


the trialkyl borines and ammonia are also formed by the boranes and ammonia; for example B2NH7 and B3N3H6, and their structures present an interesting problem.

14


15


A number of new reactions of diborane, B2H6 have been studied, but most closely related to the alkyl boron acids
and trialkyl borines are the compounds formed by the introduction of alkyl groups into the diborane molecule. The mono, di, tri, and tetramethyl derivatives of diborane, BH₃-BH₂-Me, BH₃-BH-Me₂, BH₂-Me-BH-Me₂, BH-Me₂-BH-Me₂, have been prepared by Schlesinger and Walker¹⁶ by treating diborane with trimethyl borine and isolating the individual compounds by fractional distillation. Using this same method, the four ethyl derivatives as well as the mono and di-n-propyl compounds, have been prepared by Schlesinger, Horvitz and Burg.¹⁷

Besides all of these organoboron compounds there is the possibility of hundreds of others being formed as intermediates in the countless number of organic reactions in which boron trifluoride has in recent years been employed as a catalyst.

The question arises, then, as to what particular interest these compounds might be besides the fascination of their peculiar properties and reactions. From the time that the first of these compounds had been prepared until quite recently there was no answer to this question and hence experi-
ments with these compounds were carried out only intermittently. With the rise of modern electronic theories of the mechanism of organic reactions and the nature of chemical bonds, however, it was expected that studies of organoboron compounds would be of value in interpreting the behavior of analogous electronic systems associated with carbon, since boron and carbon are so closely related in so far as effective nuclear charge and atomic radius are concerned.

In the development of these current electronic theories of organic reactions, molecules are considered to react because of an affinity either for electrons or for atomic nuclei. In order to classify reagents on the basis of the behavior of their active centers towards those of other reagents, Robinson\textsuperscript{18} and Ingold\textsuperscript{19} have designated them as electron accepting (cationoid or electrophilic) and electron donating (anionoid or nucleophilic). In general the final classification of a molecule, atom or ion has been based upon a consideration of the net result of a reaction with no regard for the electronic mechanism of the reaction. For a consideration of these reaction mechanisms, however, it is not sufficient to merely recognize the type of electro-

\begin{flushright}
\textsuperscript{18} Robinson, "Outline of an Electrochemical (Electronic) Theory of the Course of Organic Reactions", Institute of Chemistry of Great Britain and Ireland, 1932

\end{flushright}
affinity of the active centers of the reactants since an electron seeking reagent may react by the direct acquisition of electrons or it may acquire additional electrons (or a larger share in the electrons of a covalent bond) by indirect means involving a temporary electron depletion.\textsuperscript{18}

\textsuperscript{18} H.R. Snyder, J.A. Kuck, J. R. Johnson, \textit{op. cit.}, 105.

There is at present evidence to support the view that many typical reactions are initiated by the formation of unstable coordination complexes. The theory proposed by Meerwein\textsuperscript{19} as an improvement on that of Alfred Werner may be summarized briefly as follows. The atom is considered as being spherical, homogeneous, and of a definite size, the property of attraction emanating from the center of the atom and being evenly distributed over its surface. Before the reaction there is no division of this force but an atom such as carbon can attract and hold four other atoms or groups of atoms. If four atoms combine with the carbon atom,
they distribute themselves so as to produce the greatest possible neutralization of their reciprocal affinities, and the surface attraction of the carbon divides itself among the various atoms according to their nature. If all four atoms attached to the carbon atom are similar (as in CH₄), they will require an equal amount of surface attraction and will therefore arrange themselves around the center so as to form a regular tetrahedron. If any of the four atoms in union with the carbon atom are different, distribution of affinity will be irregular. If all are different an asymmetric tetrahedral grouping of the atoms will result. For example, consider an atom, Me, attached to several atoms, among which is atom X, by means of single unit valencies. If the character of this union with the other atoms engages a large fraction of the total affinity it follows that Me will have less affinity available for saturating the valence of X. The valence of X will not be fully neutralized by its union with Me and a fraction of the affinity which remains free may function as a partial valence in the formation of molecular compounds such as Me.....XA. As an example of this, triphenyl methyl chloride reacts with magnesium chloride to form addition compounds of the type (C₆H₅)₃CCl...MgCl₂. The chlorine of MgCl₂ is so active in this case as to enter into combinations with water, ethyl alcohol, and others. The residual affinities of the original addition compounds are termed auxiliary valences and are met with in the case of such radicals as are capable of functioning as whole
molecules. Trimethyl borine, \((\text{CH}_3)_3\text{B}\), exhibits such properties and thus is capable of forming coordination complexes.

Owing to the absence of unshared electron pairs or multiple bonds within the molecule, trimethyl borine affords an example of a system in which the typical reactions can occur only through the intervention of electrons from the donor center of a reagent. In order to initiate reactions of \((\text{CH}_3)_3\text{B}\) or any of the other Alkyl borines, a coordination process may take place in which the open sextet of the three-covalent boron atom acts as the electron-accepting center, or a transient "hydrogen bridge" involving the H-C link of an alkyl group may be formed. The two modes of attack are represented graphically in formulas I and II, where \(Y\) represents the active donor center of a reagent.

\[
\begin{align*}
\text{X-Y:} & \quad \text{CH}_3 \\
\text{I.} & \quad \text{X-Y:} \rightarrow \text{B} - \text{CH}_3 \\
\text{CH}_3 & \\
\text{II.} & \quad \text{X-Y:} \rightarrow \text{H-CH}_2-\text{B} \\
\text{CH}_3 & \\
\end{align*}
\]


At present very little is known of the factors governing the actual formation of these reactive complexes or the nature of the transpositions which occur within them. In some instances, as shown above, analogies may be drawn from the known behavior of relatively stable inorganic complexes, but the more significant examples are often complexes whose stable counterparts are unknown. Further difficulties arise from the fact that many molecules are capa-
ble of functioning either as an electron donor or acceptor or of offering two different points of attack to an external donor or acceptor center.

In the search for other possible electronic interpretations of typical organic reactions, mechanisms have been postulated in which an unstable configuration of six electrons (open-sextet) is regarded as the driving force of the reaction. Whitmore\(^2\) outlines some of the fundamentals of these theories as originally suggested by Carothers\(^2\) and others. We may consider an organic molecule represented electronically by \(A:B:X: \), in which \(X\) is usually oxygen or halogen or other strongly electronegative atom and \(A\) and \(B\) are atoms such as carbon, nitrogen, or boron which are neither strongly electronegative nor strongly electropositive. Each of the atoms retains a complete octet of electrons, linking being due to shared electrons. Such a molecule is very stable and relatively inactive as long as the octets are complete. If such a molecule is brought into a reaction which results in the removal of \(X\) from its attachment to atom \(B\), then regardless of the mechanism of the process, \(X\) keeps a complete octet of electrons and leaves


B with only a sextet of electrons. Thus the structure becomes :\( \vdots A;\vdots B; \vdots X; \vdots \). Three possible reactions may now occur. First, the positive organic radical may combine with a negative ion \( Y \),

\[
: A: B + : Y: \rightarrow : A: B: Y:
\]

This reaction is considered normal. Second, if the atom \( A \) has a hydrogen attached to it the fragment can be stabilized by the loss of a proton

\[
\overset{H}{A} B \rightarrow B^+ + : A: : B:
\]

hence the production of an unsaturated compound. This is also considered as being a common reaction. Third, the nature of \( A \) and \( B \) may be such that \( B \) has a greater attraction for electrons or that \( A \) can more readily dispense with a pair of its electrons. In either case \( A \) is left with an open sextet of six electrons

\[
: A: B \rightarrow : A: : B; : A: B:
\]

The new compound can then recombine with the ion \( X \) or with a new ion \( Y \) from the reaction medium, resulting in a complete rearrangement. The result is an abnormal or rearranged product.

\[
\]

Since these fugitive intermediates cannot be isolated and examined independently, the validity of these theories cannot be tested directly. However, organic derivatives of 3-covalent boron afford examples of structures containing an open-sextet of electrons and offer a means of studying the behavior of a simple acceptor (nucleophilic) center toward typical chemical reagents.\(^{23}\)

---

\(^{23}\) H.R. Snyder, J. A. Kuck, J. R. Johnson, \textit{op. cit.}, 105.

Although the organo boron compounds have served admir-
ably as test materials to substantiate these theories, they have also introduced further complications. Consider the relation of these compounds to the hydrides of boron. As has already been stated the simplest hydride of boron which enjoys stable existence is diborane, $\text{B}_2\text{H}_6$. This would appear remarkable at first sight since boron forms a number of stable compounds such as boron trifluoride $\text{BF}_3$ and trimethyl borine $\text{B(CH}_3\text{)}_3$, the molecules of which each contain a single trivalent boron atom. Moreover, the formula $\text{B}_2\text{H}_6$ implies the existence in the molecule of not fewer than seven chemical bonds of one type or another, whereas the two boron and six hydrogen atoms possess only twelve valence electrons. It is evident that diborane cannot have a simple structure such as that of ethane $\text{C}_2\text{H}_6$, in which the seven covalent bonds, each involving the sharing of two electrons, require fourteen valence electrons in all. Similar difficulties are encountered in formulating the structure of the other hydrides and it is clear that structural relationships of an unusual type occur throughout the group. The assumption that a stable structure occurs when the outer electron shell of the boron atom contains six electrons instead of the more usual eight seems quite reasonable in view of the occurrence of sextets of electrons in the other boron compounds such as the trialkyls. The "sextet" idea, however, has failed to supply a structure which accounts satisfactorily for the properties of diborane. Much more plausible structures for diborane have been based on the supposed
existence of "singlet links", i.e., bonds between atoms which share a single common electron, in contrast to bonds of the normal covalent type requiring the sharing of two electrons. 24

24 A.J.E. Welch, op. cit., 869-872.

Even the structure of the simple esters of boric acid such as trimethyl borate \((\text{CH}_3\text{O})_3\text{B}\), have undergone considerable investigation. Very recently X-ray diffraction data has been studied in an attempt to shed further light on the problem. Bauer and Beach have done considerable work in determining the structures and interatomic distances of organoboron compounds. 25


STATEMENT OF THE PROBLEM

With all of these investigators working in the field of organoboron compounds, attempting to prepare them, establish their structures and study their reactions in order to clear up some of the intricacies of organic reactions, it could not be hoped that any sudden light could be shed on the matter by a thesis of this nature. However, in order to have organoboron compounds with which to work, methods for their preparation must be developed and these
methods substantiated by other investigators. Work in the field of the boron hydrides and their organic derivatives is extremely difficult since most of these compounds are gases and elaborate apparatus, elegant vacuum techniques, and extreme cooling with liquid nitrogen are required. All of this is beyond the scope of a bachelor's thesis. If a greater amount of research is to be carried out on some of the organoboron compounds, however, methods must be devised whereby these compounds can be prepared using only the simplest of apparatus available to any ordinary chemical laboratory. In 1938 at Cornell University, procedures for the preparation of several organoboron compounds were developed which seemed to meet this requirement. The investigators reported the constants, properties, and reactions of some of the compounds which they had been able to prepare. It was deemed advisable to attempt to duplicate, in as simple a fashion as possible, their preparation of Butane boronic acid and tri-n-butyl borine. The methyl borate required in the preparation of butane boronic acid has in the past been prepared mainly by a rather difficult procedure requiring the use of an autoclave. An attempt was therefore also made to design a simple procedure for the preparation of methyl borate in good yields, and of such purity as to enable its use in the preparation of Butane boronic acid. Since most of the
necessary reagents could not be stored for any length of time due to their instability, and since it was desired to illustrate the fact that organoboron compounds can be prepared starting only with basic laboratory reagents, all of the reagents used were either prepared in the laboratory or good methods for their preparation were designated.
EXPERIMENTAL METHODS

Commercial ether contains alcohol, water, and other impurities so that it must be purified, not only for use in the preparation of the Grignard reagent but also for its use as the solvent in the preparation of both tri-n-butyl borate and dibutyl ether. To this end 350 cc. portions of commercial ether were shaken three times in a separatory funnel with different portions of a saturated salt solution (50 per cent) using each time an amount equal to about two tenth of the volume of the ether. The ether was then allowed to stand over solid calcium chloride for at least 48 hours in order to complete the removal of water and alcohol. The ether was always kept in a flask containing 5 cc. of phosphorus pentoxide and allowed to stand several days. The ether was then distilled, the first portion being discarded since it contained water from the walls of the apparatus. A fraction distillation with a calcium chloride tube attached to the side-arm was used as the receiver, so that the rest of the ether collected could be protected from the moisture of the air at all times. The ether was used immediately after distillation in each case but it could have been stored over metallic sodium in a flask having a cork stopper. In present accidents, the distillation of large quantities of ether was avoided as far as possible. It was always distilled from a 250 cc. distilling flask using a water bath and a well sealed condenser.
Commercial ether contains alcohol, water, and other impurities so that it must be purified, not only for use in the preparation of the Grignard reagent but also for its use as the solvent in the preparation of both tri-n-butyl borine and butane boronic acid. To this end 250 cc. portions of commercial ether were shaken three times in a separatory funnel with different portions of a saturated salt solution (55 per cent) using each time an amount equal to about two-tenths the volume of the ether. The ether was then allowed to stand over solid calcium chloride for at least a day, in order to complete the removal of water and alcohol. The ether was decanted from the calcium chloride into a flask containing 15 g. of phosphorous pentoxide and allowed to stand several days. The ether was then distilled, the first portion being discarded since it contained water from the walls of the apparatus. A suction flask with a calcium chloride tube attached to the side arm was used as the receiver, so that the rest of the ether collected could be protected from the moisture of the air at all times. The ether was used immediately after distillation in each case but it could have been stored over metallic sodium in a flask having a cork stopper. To prevent accidents, the distillation of large quantities of ether was avoided as far as possible. It was always distilled from a 250 cc. distilling flask using a water bath and a well cooled condenser and
receiver, and the vapors from the collection flask were conducted over the side of the table by means of rubber tubing.26


PREPARATION OF N-BUTYL BROMIDE

N-butyl bromide was prepared by the sodium bromide method. In a three liter round-bottom flask were placed 135 cc. of water and then with stirring, 155 g. of finely powdered sodium bromide. It was found advisable to add the salt to the water in this manner in place of the reverse procedure, in order to avoid caking of the sodium bromide. Ninety grams of n-butyl alcohol were then added and gradually 200 grams of concentrated sulphuric acid. The last half of the acid was added through a dropping funnel after the flask had been connected with a reflux condenser, to prevent loss of vapors. The mixture was shaken occasionally during the addition of the sulphuric acid because of a tendency to separate into two layers and was finally refluxed for a period of two hours. The condenser was then set downward and the butyl bromide, which appeared as the clear brown upper layer in the flask, was removed by distillation, the distillation requiring about one hour. The water insoluble layer of the distillate was separated, washed first with water, then with 20 g. of cold concentrated sulphuric acid, and finally with a sodium carbonate solution, of 5 g. of sodium carbonate in 50 cc. of water. The product was separa-
ted as completely as possible from the aqueous layer, dried
over night with about 5 g. of calcium chloride, decanted from
the solid calcium chloride and distilled. The range of dis-
tillation is usually given as 101 to 104° and it is mentioned
by Adkins and McElvain\(^{27}\) that when fractionated more care-

\(^{27}\) Ibid, 152.

fully, 90 per cent of this material would boil over a range of
only 1°. It was found in this experiment that the distilla-
tion could be left to proceed of its own accord and that the
temperature remained practically fixed at 101° throughout the
distillation. The yields obtained averaged about 105 g.
Adkins and McElvain reported yields of 140 to 150 g. The
final product was a clear colorless liquid with a characteris-
tic sweet odor. It was used immediately or stored in a flask
with a cork stopper.

**PREPARATION OF THE GRIGNARD REAGENT, N-BUTYL MAGNESIUM BROMIDE**

Under the term Grignard Reagent are usually classed the
magnesium alkyl halides obtained by the action of magnesium
on the alkyl halides in the presence of anhydrous ether.
The general formula for these compounds is usually written
R-Mg-X.

The apparatus for the preparation of n-butyl magnesium bromide consisted of a one liter round-bottom flask which
was connected through a Y-tube in the cork to a reflux con-
denser and a dropping funnel. It was essential that all the
apparatus used was thoroughly dry and that all access of moisture and carbon dioxide to the reaction mixture was avoided since both of these react with and destroy the Grignard reagent. This was provided for by connecting the upper end of the condenser to a soda lime tower. It is pointed out by some chemists that the reagent is not entirely insensitive to the action of the oxygen of the air. Consequently, they prefer to exclude air by the passage of a slow current of dry hydrogen through the reaction mixture. Magnesium may be conveniently employed either in the form of filings, turnings, or ribbon. The ribbon which was used in this experiment was polished until bright with fine sand paper to remove the superficial coating of oxide, wiped clean, and cut into lengths of one to two centimeters. It was found that filings which had been stored for some time were covered with a coating of oxide and although degreased by cleaning with alcohol and ether, failed to show any reaction with the n-butyl bromide even after considerable refluxing.

Thirteen grams of the magnesium ribbon (.54 gram atom) were placed in the bottom of the flask. In the dropping funnel was placed a mixture of 60 cc. (77.9 g. or .57 mole) of anhydrous n-butyl bromide and an equal volume of anhydrous ether. About one-third of this mixture was allowed to drain into the reaction flask. After a few minutes, if the reaction did not start of its own accord, the flask was
warmed very gently until the start of the reaction was noted by vigorous bubbling even after removal of the flame. If the reaction became too violent, it was cooled down by surrounding the flask with crushed ice in a water bath. After the reaction was proceeding smoothly an additional 50 cc. of anhydrous ether were added through the reflux condenser. The remaining mixture in the dropping funnel was added over a period of one-half hour at a rate such that the mixture refluxed gently. Another 50 cc. portion of anhydrous ether was then added through the reflux condenser and the mixture was refluxed gently for another hour, until practically all of the magnesium had disappeared. The clear solution was decanted from any residual magnesium at the bottom of the flask. The solution was made up to a volume of 300 cc. to provide the necessary concentration of reagent for the preparation of butane boronic acid. In each instance the reagent was prepared the night before using and was kept out of contact with the air in a flask closed by a cork stopper.  

28

Ibid, 210

Henry Wren, The Organometallic Compounds of Zinc and Magnesium, 69.

THE PREPARATION OF BORON TRIFLUORIDE ETHERATE

Since a small amount of boron trifluoride etherate, \((\text{C}_2\text{H}_5)_2\text{O-BF}_3\), was available it was not necessary to prepare this compound for the present experiment. That this compound could easily be prepared, however, may be seen from an
examination of the method used by Johnson, Snyder and Van Campen. They prepared the etherate of boron tri-
fluoride by passing gaseous boron trifluoride into anhy-
drous ether with external cooling and fractionating the product at atmospheric pressure (b.p. 124-125° at 745 mm.). The boron trifluoride was generated in glass apparatus by the action of concentrated sulphuric acid upon a mixture of powdered boric anhydride and either potassium fluborate or calcium fluoride. Tin foil had to be used to protect the stoppers.

PREPARATION OF TRI-N-BUTYL BORINE

APPARATUS

The apparatus used in the preparation of tri-n-butyl borine is shown in plates I and II. The essential part of the apparatus, the reaction flask, was a three necked, round-bottom, one liter Wouff flask. Through the cork stopper in the center neck of the flask passed an inlet tube for nitrogen (A) and a mercury sealed stirrer. Since the reaction had to be conducted in an inert atmosphere of nitrogen gas, this type stirrer had to be employed to permit thorough mixing of the reactants and still keep the flask
gas tight.

The stirrer consisted of a 6 mm. glass rod (B) flattened into the shape of a small paddle at one end by softening in a flame and pinching with a crucible tong. The glass rod fitted into a sleeve of 10 mm. glass tubing (C) the lower end of which was fitted snugly into a hole in the cork stopper of the Woulff flask. The upper end of the sleeve passed through a rubber stopper in the mouth at the bottom of the outer jacket of the stirrer. This outer jacket consisted of a 16.2 cm. section of one end of a damaged condenser jacket, 35 mm. in diameter. This was found to be very convenient because the side tube could conveniently be used as a drain for the mercury (E) in case of trouble, adjustments, or cleaning of the stirrer. The side tube was closed by screwing on a small rubber stopper (F). A glass tube (G) 19 mm. in diameter was clamped to the center rod by means of a rubber stopper (H) and had its lower end dipping below the surface of the mercury. A metal tube or sleeve (I) 8 mm. in diameter acted as a bearing to steady the upper end of the glass rod while in motion. The sleeve was held in place by means of a cork stopper which fitted into the upper neck of the outer jacket. Both the top and bottom of the sleeve were finished off with a flattened head to prevent excess friction or sticking of the stirrer. Resting on the upper head of the sleeve was a hard rubber washer which made contact with the large grooved rubber stopper (J) acting as a drive wheel.
This wheel was connected to the wheel of the small motor by means of a small belt. The motor used was one-twentieth horsepower operating on 110 volt 60 cycle current.

Passing through the cork stopper in the left hand neck of the Woulff flask was a reflux condenser (K) which served to condense any of the solvent, ether, vaporized by the heat of the reaction. From the top of the reflux condenser an outlet tube for nitrogen passed into a trap (L) which served to collect any of the ether carried over by the stream of gas.

The cork stopper in the right hand neck of the Woulff flask contained a dropping funnel (M) and an emergency tube (N). This tube was first described as the outlet tube for nitrogen but it was found that too much ether was carried along out of the flask through this tube. By placing the outlet at the top of the condenser, any ether being carried along was condensed and dropped back into the reaction flask. The extra tube was kept in position, however, and was found to be of great use when the inlet tube for nitrogen clogged up. When not in use it was closed off with a short piece of rubber tubing and a pinch clip. The dropping funnel had a bent stem so that the reagent was introduced into the center of the flask, and the tip of the stem was drawn down.

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31 J.R. Johnson, H.R. Snyder, M.G. Van Campen, Jr., op. cit., 118.
PLATE I
APPARATUS FOR THE PREPARATION OF
TRI-N-BUTYL BORINE
PLATE II
APPARATUS FOR THE
PREPARATION OF
TRI-N-BUTYL BORINE
to a fine point so that the reagent could be introduced very slowly. The dropping funnel was closed by means of a mercury valve (O) to prevent contact with the air, allow for differences in pressure and permit addition of the reagent. By raising the tube momentarily above the surface of the mercury, the pressure above the liquid in the dropping funnel was allowed to return to atmospheric pressure, and the dropping could continue. The reaction flask was warmed by means of a water bath (P). The inert atmosphere was provided by passing nitrogen through the reaction flask, the nitrogen being supplied from a steel cylinder of 100 cu. ft. capacity (Q). The nitrogen was purified by bubbling through alkaline pyrogallol in a wash bottle (R) to remove any oxygen and then bubbling through concentrated sulphuric acid in another wash bottle (S) to remove any moisture. The alkaline pyrogallol was prepared by dissolving 4 g. of pyrogallic acid in 16 cc. of water, 28 g. of potassium hydroxide sticks in 68 cc. of water and then mixing the two solutions.

**PROCEDURE**

The procedure used for the preparation of tri-n-butyl borine, employing boron trifluoride etherate as the source of boron and the Grignard reagent, butyl magnesium bromide, as the source of the n-butyl groups was employed by Krause and Nitsche, and Johnson, Snyder and Van Campen, Jr., reported

32 Erich Krause, Rudolf Nitsche, *op. cit.*, 2784

32 J.R. Johnson, H.R. Snyder, M.G. Van Campen, Jr., *op. cit.*, 116.
excellent yields of 80% using their method. In this experiment the method described by the latter investigators was employed, using one-half of the specified quantities of reagents.

An etherial solution containing one-half mole of n-butyl magnesium bromide was placed quickly in the Woulff flask. The apparatus was swept out with a stream of purified nitrogen and a slow stream of nitrogen was passed through the apparatus for the duration of the reaction. A solution of 22.35 gm. (.155 mole) of boron trifluoride etherate in 100 cc. of dry ether was added with stirring at a rate sufficient to cause gentle refluxing. With the dropping funnel set so that this was added at the rate of about one drop every one to two seconds, the addition required two hours. The mixture was then refluxed gently on the water bath, with stirring, for an additional two hours. The mixture was cooled and a solution of 50 cc. of concentrated hydrochloric acid in 300 cc. of water was added carefully with stirring. The precipitate from the Grignard reagent disappeared leaving two clear colorless liquids; the ether layer containing tri-n-butyl borine at the top and the water layer at the bottom. Since tri-n-butyl borine is oxidized so rapidly upon contact with the air that it bursts into flame, it was necessary to devise a means of transferring the ether layer to a separatory funnel without contact with the air. This was accomplished by making use of the wash bottle principle. The stopper containing the outlet
tube for nitrogen and the dropping funnel was replaced very quickly with a stopper containing a single long glass tube. This tube was connected by means of a short piece of rubber tubing to another glass tube extending slightly below the bottom of a stopper placed in the top of a separatory funnel. Another glass tube extending flush with the bottom of the stopper served as an outlet tube. Nitrogen was allowed to pass through and flush out this system. The long glass tube in the right neck of the reaction flask was then pushed down through the stopper until it came in contact with the surface of the ether layer. The incoming nitrogen gas then having no means of escape from the flask exerted pressure on the surface of the liquid forcing it up the tube and over into the separatory funnel. As the liquid was removed, the long glass tube was lowered until its tip just came in contact with the interface of the two layers and all the upper layer had been removed. Both the inlet and outlet tubes of the separatory funnel were closed off by means of short pieces of rubber tubing and pinch clips. A wash bottle was constructed so that wash solutions could be forced over into the separatory funnel by means of nitrogen pressure. In this manner the ethereal solution was washed with water, 5% sodium bicarbonate solution and again with water. The wash solution became the bottom layer in each instance and was easily drained out through the stem of the funnel. After the stem had drained out thoroughly, the funnel was inserted through a hole in the stopper of an
Erlenmeyer flask containing a small amount of anhydrous magnesium sulfate as drying agent, and the ethereal solution was run in and allowed to stand overnight in the stoppered flask. The ethereal solution was then decanted through a tube out of contact with the air into the 500 cc. Claisen flask (A) in plate IV and the ether was distilled off on the water bath.

**THE VACUUM DISTILLATION OF TRI-N-BUTYL BORINE**

After distilling off the ether it became necessary to distill off the tri-n-butyl borine under reduced pressure to avoid decomposition. The apparatus for this distillation is shown in plates III and IV. The Claisen flask (A) contained a thermometer (B) and a long tube (C) drawn to a fine point which extended beneath the surface of the liquid in the flask. In order to provide an inert atmosphere and also to promote smooth boiling, nitrogen was passed through this tube. The nitrogen after being purified by bubbling through alkaline pyrogallol and concentrated sulphuric acid was passed through a glass coil (D) immersed in hot water so that the gas would be warmed up before entering the distillation flask. The collection flask (E) was cooled by allowing water from the tap at (F) to flow over it, the water being caught by a large funnel and returned to the sink. The side-arm of the collection flask was connected to a trap (H) by means of heavy tubing. Also connected through the stopper of the trap was one arm of an open tube mercury manometer (I) used to register the pressure under which the distillation took place. The
PLATE III
APPARATUS FOR THE VACUUM DISTILLATION OF
TRI-N-BUTYL BORINE
PLATE IV
APPARATUS FOR THE VACUUM
DISTILLATION OF TRI-N-BUTYL BORINE
side arm of the suction flask serving as a trap was connected to a tube extending into another suction flask (J) filled with a mixture of soda lime and calcium chloride drying agents, to protect the pump. Through another hole in the stopper of the flask passed a small safety tube closed by means of a short piece of rubber tubing and a screw clamp. By opening or closing the clamp the amount of suction could be controlled and any sudden sucking back was prevented. In order to produce the low pressure, a Cenco Megovac pump was used, operated by a one horse power, single phase, motor drawing seven amperes of a 220 volt 60 cycle current.

After all of the ether had been distilled over, the solution in the Claisen flask was allowed to cool somewhat. A new receiver was quickly put into place and the vacuum pump was put into operation. The Claisen flask was heated gently with a Bunsen burner. When the temperature reached 90° C, the distillation began but the temperature continued to rise to 94°. The barometric pressure was 751 mm. of Hg. and the manometer registered 740 mm. indicating that the pressure in the system was 11 mm. Later the temperature dropped down to 90° C and upon checking the manometer it was found that the pressure had dropped to 9 mm. The pressure then varied between nine and ten millimeters of mercury but the liquid kept distilling over at 90°. The distillation was stopped when the temperature began to rise rapidly.

The product obtained was transferred immediately to a small nitrogen filled flask which was stoppered and placed in
a large nitrogen filled dissicator. When the flask was removed momentarily from the dissicator and opened in order to remove a sample, the temperature rose rapidly and the flask became very warm to the touch. The product was a colorless mobile liquid which was found to undergo oxidation rapidly in air. One or two cc. of the liquid were poured on a cotton cloth; within about five seconds clouds of white vapor arose and the cloth burst into green flames a foot high.

When a few drops of the purified tri-n-butyl borine in 95% ethyl alcohol were added to an aqueous solution of picric acid in a test tube and warmed, the solution turned from a light yellow to a deep orange or red. Johnson, Snyder and Van Campen found this color reaction to be the only distinctive one given by tri-n-butyl borine.

33


They also reported that attempts to prepare a solid addition product of the borine were unsuccessful and that no precipitate was formed and no heat generated when a solution of tri-n-butyl borine in ethanol or benzene was mixed with solutions of the following substances: aniline, methyl aniline, p-nitroaniline, p-anisidine, dimethyl amine, tri-ethyl amine, p-toluenesulfonic acid, thio-p-cresol, picric acid.

REATIONS OF TRI-N-BUTYL BORINE

Johnson, Snyder and Van Campen have made quite a thorough study of some of the reactions which tri-n-butyl borine
undergoes. Perhaps the most interesting of these are the
oxidation reactions. It has already been mentioned that the
trialkyl borines react vigorously with atmospheric oxygen and
that the lower members of the series, such as tri-n-butyl
borine, are spontaneously inflammible in the air. In the
absence of water and upon slow admission of air, tri-n-butyl
borine is oxidized to the n-butyl ester of 1-butane boronic
acid. Johnson and Van Campen were able to isolate this com-
 pound in pure form. In this reaction one mole of tri-n-butyl
borine requires one mole of oxygen and the oxidation is clear
cut with no evidence of any other reaction. Upon hydrolysis
of the resulting compound, butane boronic acid and two mole-
cules of n-butyl alcohol are produced.

\[
\text{C}_4\text{H}_9\text{B} + \text{O}_2 \xrightarrow{\text{Air, Anhydrous Conditions}} \text{C}_4\text{H}_9\text{B} \quad + \quad 2\text{H}_2\text{O} \xrightarrow{\text{Acid}} \text{C}_4\text{H}_9\text{B} + 2\text{C}_4\text{H}_9\text{OH}
\]

If the reaction is carried out in the presence of water,
however, but still using air as the source of oxygen, the
oxidation process consumes only one-half mole of oxygen and
is arrested neatly at the half way stage. The same investi-
gators isolated the n-butyl ester of di-n-butyl borinic acid
in 92% of the theoretical amount.
This observation suggests that anhydrous autoxidation is a stepwise process in which the dialkylborinic ester is an intermediate product and that water inhibits the further oxidation of the latter.

Frankland's observation that the ammoniate of trimethyl borine is stable toward atmospheric oxygen, and other indirect evidence, supports the hypothesis that autoxidation proceeds by way of an intermediate complex in which the oxygen molecule acts as electron-donor. The primary adduct or unstable "borine-peroxide" (I) then reacts with a second molecule of the borine to produce two molecules of the dialkylborinic ester (II) in a manner analogous to the interaction of peracetic acid and acetaldehyde to give two molecules of acetic acid.

\[(I) R_3B + O_2 \rightarrow R_3B = O \quad \text{and} \quad (II) R_3BO_2 + R_3B \rightarrow 2R_2BOR \]

J.R. Johnson, H.R. Snyder, M.G. Van Campen, Jr., op. cit., 117.

Aqueous hydrogen peroxide in the presence of dilute alkali causes complete dealkylation of tri-n-butyl borine with the formation of boric acid and n-butyl alcohol.

\[C_4H_9B\left(C_4H_9\right) + 3H_2O_2 \rightarrow H_3BO_3 + 3C_4H_9OH\]

This reaction is rapid and quantitative and is used for the determination of boron in organoboron compounds. If benzoyl peroxide or perbenzoic acid in a chloroform solution is added to tri-n-butyl borine, the cleavage of all three alkyl groups results. Three moles of perbenzoic acid are reduced per mole of the borine and the reaction is practically
Another series of interesting reactions is given with bromine and hydrogen bromide. With anhydrous HBr the quantitative cleavage of one alkyl group results. With concentrated aqueous HBr the initial reaction is the same but the presence of water carries the reaction several steps further, going from the bromide to the borinic acid and then to the oxide.

Anhydrous bromine produces similar results and to a limited extent two alkyl groups can be removed from boron with
The behavior of the alkyl boron compounds toward hydrogen bromide, bromine, perbenzoic acid, hydrogen peroxide, and molecular oxygen indicates a definite gradation of reactivities. Clevage of the boron-alkyl linkage occurs less readily as the alkyl groups of the borine are replaced successively by halogen, hydroxyl or alkoxy groups. 36

J.R. Johnson, M.G. Van Campen, Jr., op. cit., 124.

The following summary of decreasing activity of the alkyl organoboron compounds can then be given:

\[
R_3B > R_2BX > RBX_2 \\
R_3B > R_2BOH > RB(OH)_2 \\
R_3B > R_2BOR > RB(OR)_2
\]

From these gradations in activity it would seem that the reactivity of the alkyl organoboron compounds toward a given donor molecule is diminished by the attachment of atoms or groups which contain unshared electron pairs ( -Br, -OH, -OR ) and are capable of giving rise to resonance effects.
APPARATUS

The apparatus for the preparation of butane boronic acid is somewhat similar to that used for the preparation of tri-n-butyl borine and is shown in plates V and VI. Since the reaction was controlled at low temperatures, very little ether vapor was present and a low temperature thermometer was substituted for the reflux condenser used in the preparation of tri-n-butyl borine. Instead of a water bath to warm the reaction mixture, dry ice and acetone in a Dewar vessel were used to cool it. The apparatus consisted, therefore, of a three-necked, round bottom, one liter Woulff flask (A), the center neck being stoppered with a cork containing an inlet tube for nitrogen (B) and the mercury sealed stirrer (C). The right neck was stoppered with a cork containing an outlet for nitrogen (D) and the dropping funnel (E) with the stem bent toward the center of the flask but with a slightly larger opening at the tip to permit better flow, since it was found that the dropping funnel tended to clog at the low temperatures of the reaction. It was found that if the reagent was introduced against the side of the flask, the voluminous precipitate settling out tended to clog the funnel still more and seriously impaired the stirring. These difficulties were also encountered by Snyder, Kuck and Johnson\(^{37}\) and were overcome by using the bent stem so that the reagent was introduced at the center of the flask. The dropping funnel was again

closed by means of a mercury valve (F) to exclude contact with the air, allow for differences in pressure and permit the dropping in of the reagent. In the left neck of the Woulff flask was a cork through which passed a low temperature thermometer reading from $50^\circ$ C to $-100^\circ$ C. Corks were used both because of the etherial solution and to prevent hardening which rubber stoppers undergo at very low temperatures. The outside of the corks was coated with collodion to prevent leakage of the nitrogen.

The inert atmosphere was again provided by passing nitrogen through the reaction flask and the nitrogen was again purified by passing through alkaline pyrogallol and concentrated sulphuric acid. In the photograph, Plate V, the gas purification chain is shown at the left, while in the drawing, Plate VI, only the tube B through which the gas enters the reaction flask is shown. At D in the drawing the gas leaves the reaction flask and it can be seen from the photograph that it then passes through a trap which can collect any condensed vapors carried over from the reaction flask, and keeps the outlet from the flask in contact directly with another atmosphere of nitrogen rather than air.

It was found very convenient to use as the cooling chamber a Dewar vessel which ordinarily serves as the insulating jacket for the bomb calorimeter. The diameter of the vessel was 15 cm., large enough to admit freely the 12 cm. diameter one liter Woulff flask and permit dry ice to be placed above, below and
PLATE V
APPARATUS FOR THE PREPARATION OF BUTANE BORONIC ACID
PLATE VI
APPARATUS FOR THE
PREPARATION OF BUTANE BORONIC ACID
around the flask. The calorimeter jacket consisted of a regular Dewar vessel (G) around which was packed a layer of felt insulating material (H), the whole being supported in a cylindrical metal shell (I). When in use the mouth of the Dewar vessel was covered with strips of felt to shut out warm currents of air.

PROCEDURE

The procedure used for the preparation of butane boronic acid was that which was successfully employed by Snyder, Kuck and Johnson, as an adaptation of the procedures first used by Khotinsky and Melamed. The source of boron was methyl borate.

On the basis of the yields obtained by Snyder, Kuck and Johnson, this reagent proved most suitable being better than the n-butyl borate preferred by Bean and other investigators because of the greater ease of its preparation since methyl alcohol free methyl borate is considered extremely difficult to prepare. The source of the n-butyl group was again the Grignard reagent, n-butyl magnesium bromide.

The apparatus was assembled as shown in plate V and dry nitrogen was allowed to flow through it for 15 minutes. Mean-
while, dry ice had been placed at the bottom of the Dewar flask and was piled around the reaction flask, a small amount of acetone being poured on the dry ice from time to time to still further reduce the temperature. Then 55 gm. or 0.53 mole of pure methyl borate was added quickly through the separatory funnel and was washed through with 150 cc. of anhydrous ether. The solution was stirred until cooled below $-70^\circ$ C. This required at least two hours. Next 300 cc. (0.5 mole) of n-butyl magnesium bromide solution (1.66 N.) was introduced slowly through the separatory funnel over a period of 6 hours. The flow of nitrogen and stirring were continued and the temperature was kept below $-60^\circ$. The addition of the n-butyl magnesium bromide solution could not be hastened since the temperature kept rising with larger additions due to the heat given off by the reaction. To facilitate the dropping, the tube in the mercury valve was lifted above the surface of the mercury from time to time thus allowing atmospheric pressure to act on the surface of the liquid in the dropping funnel. After the addition was completed the mixture was stirred for four hours longer, the temperature finally dropping down below $-70^\circ$ C. The mixture was then allowed to stand in the cooling bath for the rest of the night. After about eight hours the temperature in one case was still at $-76^\circ$ and after removing all insulation from the mouth of the Dewar vessel and allowing to stand for another two hours the temperature had only warmed up to $-60^\circ$. The larger pieces of dry ice packed around the top of the flask were then removed and a stream of air was blown into the Dewar dish carrying along
out the cold heavy carbon dioxide vapor. After about one hour
the temperature had warmed up to \(-20^\circ C\). The reaction mixture
consisted of a heavy, "taffy-like" precipitate covered by a
clear liquid. In order to carry out the hydrolysis of the two
methoxy groups from the boron atom, 300 cc. of water containing
30 cc. of sulphuric acid was then added fairly rapidly from
the dropping funnel with stirring and cooling and the small
amount of heat given off in the hydrolysis along with the rela-
tive warmness of the liquid being added brought the temperature
of the reaction up to \(10^\circ C\). The flask was then removed from
the ice bath and allowed to come to room temperature.

The ethereal layer was removed in the same manner as in
the preparation of tri-n-butyl borine, using nitrogen pressure
to force the layer up through an outlet tube in wash bottle
fashion. The water layer was extracted with ether twice, being
divided up into three portions each time and about 20 cc. of
ether being used for each portion. This ether extract was com-
bined with the main portion.

Using a 250 cc. distilling flask and a steam bath, the
etherial solution was concentrated by distilling off the ether.
Twenty cc. of water was then added and the distillation was
stopped when all the material volatile at the temperature of
the steam bath had apparently distilled over. On cooling the
residual liquid with an ice salt bath, however, no crystals
formed. The suction flask being used as a receiver was connect-
ed to a water aspirator and the solution in the distilling
flask was concentrated further by vacuum distillation on the
steam bath. A brown oily layer remained on top of the solution and later clear oily drops appeared on the surface of the distillate. After the solution had been concentrated further and left to stand for a day, a few colorless crystalline needles were found suspended from the surface of the liquid. The solution was cooled down with ice water and clusters of very fine, light, colorless crystals settled down in a manner resembling snow flakes. When the solution warmed up to room temperature, however, a portion of these crystals had evidently redissolved.

A small amount of the crystalline substance was dissolved in a solution of silver nitrate in a test tube to which dilute ammonium hydroxide had been added until the precipitated oxide redissolved. The solution was then warmed and finally boiled for ten minutes under a reflux condenser. At the end of this time the solution was filled with shining silver splinters showing that the butane boronic acid had reduced the ammoniacal silver nitrate. This reaction is described by Johnson, Van Campen and Grummitt. 41


In order to recrystallize the product, all of the water was first removed by vacuum distillation on the water bath. Enough toluene was then added to dissolve all of the crude acid. When warmed, and the solution was filtered through a hot water funnel. Upon thorough chilling of the solution, the acid separated out in very fine needles. It proved convenient
to store the acid in the crude moist condition and to purify samples only as needed, since the dry purified samples must be excluded from contact with air, but the moist specimens do not suffer auto oxidation.

Some difficulty was encountered in attempting to determine the melting point of specimens of butane boronic acid. If the specimens were too moist no actual melting point could be obtained since the acid is soluble in hot water. While if the specimens were too dry, they were evidently converted into the oxide before the melting point was reached. A method was finally devised in which the moist crystals were allowed to dry in an atmosphere of nitrogen and the melting point was actually determined in this atmosphere. The melting point apparatus consisted of a test tube with the bottom end drawn down to a fine capillary about 3 cm. long and sealed off. The mouth of the tube was closed by a two holed rubber stopper through which passed an inlet and outlet tube for nitrogen. Moist crystals were placed in the tube and forced into the capillary. Nitrogen was then passed through the test tube until the crystals were fairly dry and a very slow stream of the gas was passed through during the melting point determination. The temperature of the sulphuric acid bath was raised rapidly to 80° C. and then at the rate of about one degree a minute until the melting point was reached. In this manner samples of the product crystallized from water or toluene appeared to melt at 90° C. Several samples, however, did not melt although the temperature was raised above 120° C. Samples heated above
100° showed a vigorous effervescence.

**REACTIONS OF BUTANE BORONIC ACID**

It has already been pointed out that water does not inhibit the autooxidation of trialkyl borines but is effective for compounds containing an alkoxy or hydroxyl group attached to boron. Thus free aliphatic boronic acids such as butane boronic acid undergo oxidation in dry air but are unaffected when moisture is present. It is believed that the inhibition mechanism involves the presence of the linkage \(-\text{B-O-}\) and it is possible that the ability of these compounds to form more stable hydrates than the borines is responsible for arresting the autooxidation. The organoboronic acids were first expected to form double molecules in a manner similar to alcohols and carboxylic acids, but Kinney and Pontz\(^{42}\) have shown that freshly crystallized organoboronic acids do not


associate in nitrobenzene and that in this solvent there is no appreciable amount of hydrogen bond formation. When the organoboronic acids dehydrate under atmospheric conditions, however, the resulting organoboron oxides show an increase in their molecular weights, indicating that the organoboron oxides do not have the simple boronyl structure \(\text{RBO}\) arbitrarily assigned to them. In their work Kinney and Pontz\(^{43}\) prepared

the oxides by heating the corresponding boric acid derivatives for thirty three hours in a drying oven at 110°. When the products were analyzed and their molecular weights determined cryoscopically in nitrobenzene, the values indicated probable mixtures of double, triple and even higher molecular weight oxides. In comparing the structures to boric anhydride in which at least one oxygen linkage is present (O=O-O=O) the following cyclic formulas analogous to paraldehyde were suggested in place of merely associated molecules.

Another important reaction is the reducing action exhibited by the organoboronic acids. Michaelis and Becker44 first

44 A. Michaelis, P. Becker, op. cit., 182.

reported the formation of a silver mirror when benzene boronic acid was warmed with silver nitrate in ammoniacal solution and observed that benzene was the principal organic product of the reaction. The reaction with ammoniacal silver oxide is actually a hydrolytic cleavage and not a reduction.

\[ C_6H_5(OH)_2 + HOH \overset{\left\{ Ag\left(NH_3\right)\right\}^+}{\rightarrow} C_6H_5-H + H_3BO_3 \]

The production of silver is not accounted for in this reaction and very little is really produced. Johnson, Van Campen and Grummitt45 found that the aliphatic boronic acids such as

45 J.R. Johnson, M.G. Van Campen, Jr., Oliver Grummitt, op. cit., 111-115.
butane boronic acid reduce silver nitrate in ammoniacal solution with the production of one equivalent of metallic silver and the hydrocarbon R-R. It was suggested that the reduction of ammoniacal silver oxide by aliphatic boronic acids involves the formation of an unstable silver alkyl.

**THE PREPARATION OF METHYL BORATE**

Methyl borate, the tri methyl ester of boric acid, would seem to be relatively easy to prepare, and yet this reagent has been considered exceedingly difficult to prepare in the pure form and has proved to be one of the headaches of all of the chemists who have found its use necessary in the preparation of the boronic acids. In this experiment an attempt was made to devise a shorter, simpler, less expensive method for its preparation than that used by a majority of the experimenters in the past. Khotinsky and Melamed\(^\text{46}\) reported using Shiff's method for the preparation of all the boric acid esters used in their experiments. This method consists in heating the corresponding alcohol with boric anhydride in an autoclave for several hours. Boric anhydride reacts with methyl alcohol at 100° to 120° C. in an autoclave to form methyl borate but upon further heating of the methyl borate in the presence of boric anhydride, the meta borate is formed.\(^\text{47}\)

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\(^{46}\) Eugene Khotinsky, M. Melamed, *op. cit.*, 3091.

This is a tedious, rather difficult procedure and still does not solve the problem of purifying the methyl borate produced. Beilstein\textsuperscript{48} lists several other procedures which present further difficulties in that the preparation of still other reagents is required. For example, if the method of dropping boron trichloride, $\text{BCl}_3$, into methyl alcohol were used, the boron trichloride would also have to be prepared. The reaction of the disulfate, $(\text{SO}_3)_2\text{B}_2\text{O}_3$, and methyl alcohol or the reaction of dimethoxy boron fluoride, $(\text{CH}_3\text{O})_2\text{BF}$ or methoxy boron difluoride, $\text{CH}_3\text{OBF}_2$ and sodium methylate were also discarded as not being too practical. Gmelin\textsuperscript{49} lists several additional methods such as the reaction of methyl alcohol with the mixed anhydride of boric and acetic acids or boron triacetate and the distillation of alkyl sulphates with hydrated borax. He also mentions the fact that alcohols will react with fused, finely powdered boric acid in the presence of $\text{HCl}$ or concentrated sulphuric acid. This method seemed the simplest and most logical, if good yields could be obtained. In 1929, however, Khotinskii and Pupko,\textsuperscript{50} developed

\begin{thebibliography}{99}
\bibitem{48} Bernhard Prager, Paul Jacobson, \textit{Beilsteins Handbuch der Organischen Chemie}, 1:287.


\end{thebibliography}
another interesting method. They offered fused borax for the reaction of esterification, which was then thought to proceed as follows:

$$3 \text{Na}_2 \text{B}_4 \text{O}_7 + 6 \text{HCl} + 15 \text{C}_2 \text{H}_5 \text{OH} \rightarrow 6 \text{NaCl} + 5 \text{B(OC}_2 \text{H}_5)_3 + 7 \text{H}_3 \text{BO}_3.$$ 

Their experiments seemed to indicate this as a general method to be employed in the laboratory for preparing small amounts of boric esters without the aid of an autoclave. Details of their procedure were not available, but an application of the general principles to the preparation of methyl borate gave very impure yields.

In 1936 Arquet\textsuperscript{51} reported that 68\% of a quantity of H\textsubscript{3}BO\textsubscript{3} was lost by spontaneous evaporation in a 99.5\% methyl alcohol solution overnight. Thus he was led to believe that the esterification took place at room temperature even without the addition of a mineral acid. It was therefore resolved finally to use the regular method of ester formation of an alcohol plus an acid in the presence of a dehydrating agent such as sulphuric acid.

One difficulty arose and that was the fact that boric acid is a solid and yet in the regular procedure such as the preparation of ethyl acetate the acid is usually dropped into the reaction flask. To accomplish this the regular dropping funnel was replaced by a 300 cc. Erlenmeyer flask, shown at (A) in plate VII. One end of the tube was attached to a large

\textsuperscript{51} Maurice Arquet, "Volatilization of Boric Acid in the Cold by Vapors of the Lower Members of the Primary Alcohols," \textit{Bulletin de la Société Chimique de France}, 1936, (5) 3:1422-4.
stop cock (B) which passed through a rubber stopper in the mouth of the Erlenmeyer, while the tube at the other end was connected to one arm of a Y tube. The other arm of the Y tube was closed off by means of a short piece of rubber tubing and a pinch clip (C). The base of the Y tube was connected to a long glass tube 10 mm. in diameter which reached down below the surface of any liquid in the distilling flask (D). Also dropping beneath the surface of the liquid was a thermometer (E). The distilling flask was connected to a condenser and a suction flask served as a receiver. The side arm of the suction flask was connected to a calcium chloride tube to keep the product dry, since methyl borate is easily decomposed by the moisture in the air.

In the distilling flask were placed 49 grams (.5 mole) of concentrated sulphuric acid and 16 grams (.5 mole) of absolute methyl alcohol. In the Erlenmeyer flask were placed 61.8 grams (1 mole) of very finely powdered anhydrous boric acid and 106 grams (3 mole plus 10% excess) of absolute methyl alcohol. The mixture was shaken well to produce a fine suspension of the boric acid in the alcohol. The stopper containing the stop cock was then wired onto the neck of the flask and this was connected to the train of apparatus. The mixture in the flask was heated up to 120° and the material in the dropping flask was then slowly dropped into the reaction flask over a period of two hours. During this time the temperature of the reaction mixture was kept at about 120° C. and the receiver was well packed in
ice. The boric acid-methyl alcohol suspension was shaken from time to time to keep it uniform. If there was a tendency for the liquid to back up the dropping tube, the pinch clip on the safety valve was merely opened carefully for a moment, atmospheric pressure forcing the liquid back down into the flask. When an attempt was made to prepare larger quantities than this at one time, it was found that the inlet tube clogged and the reaction had to be stopped while this tube was cleaned out. Sixty-eight grams (65% of the theoretical amount) of crude methyl borate was obtained in this manner.

The question of obtaining pure methyl borate still remained, however. The absolute necessity of having pure methyl borate for the preparation of such compounds as butane boronic acid was emphasized by Seaman and Johnson who found that the presence of methyl alcohol in the methyl borate caused a great diminution in the yields of such compounds as phenylboric acid, the losses apparently being greater than could be accounted for on the basis of the Grignard reagent actually destroyed by the alcohol. To remove the last traces of alcohol, they employed the method of Shiff which consists in washing with cold concentrated sulphuric acid. In this experiment the flask containing the crude methyl borate was chilled in an ice bath and concentrated sulphuric acid was added very slowly in small amounts...
until sputtering no longer occurred. This sputtering was the same as that produced when sulphuric acid was added to and reacted with pure methyl alcohol. An addition of 10 cc. of sulphuric acid was usually required before no further reaction was apparent. The methyl borate was removed from this mixture by distillation, the majority of the product distilling between 67° and 70° C. Only 3 cc. distilled over below 65° but even this fraction showed a bright green flame, characteristic of methyl borate when its vapors were burned. The fraction coming over from 80° to 95° amounted to 10 cc. and this burned with a very feeble green flame indicating that some water and other impurities were probably present. The fraction coming over between 65° and 80°, with about 85% coming over between 67° and 70° burned with a bright green flame and decomposed leaving a white film of boric acid when exposed to the moisture of the air. This fraction weighed 40.7 gm., a yield of 39.1%.
DISCUSSION OF RESULTS AND CONCLUSIONS

When all of the necessary techniques had been mastered the preparation of tri-n-butyl borine proceeded very smoothly. Due to an accident in which about half of the final yield was lost during the vacuum distillation, no significant percentage yield could be calculated for the experiment. Even the yield which was obtained, however, indicated that with the proper experience very good yields could be obtained. Practically all of the tri-n-butyl borine obtained distilled over at 91° C. under a pressure of 9 mm. This boiling point is in excellent agreement with the data given by Johnson, Snyder and Van Campen who reported boiling points of 90° - 91° at 9 mm. pressure or 108° - 110° at 20 mm. The substance was a perfectly colorless mobile liquid with the peculiar, very pronounced odor best described by Krause and Nitsche.

"Die nunmehr analysenreinen Boralkyle sind farblose, leicht bewegliche Flüssigkeiten von nicht allzu unangenehmen, characterischen Geruch, der teils on tertiäre Alkylphosphine, teils on Rettich und Zwiebel erinnert."

The tri-n-butyl borine was oxidized spontaneously in air, bursting into green colored flames when placed on a cotton cloth exactly as described by Johnson, Snyder and
The picric acid color reaction reported by these investigators was also verified.

If for any reason the liquid tri-n-butyl borine was exposed to the air for a very short time, the flask containing it immediately became warm. Johnson, Snyder and Van Campen placed some of the liquid in an open beaker and observed that the temperature rose rapidly to 90° C.

The crystalline butane boronic acid obtained, corresponded to the description given by Krause and Nitsche.

"Farblose, längliche, an beiden Enden dachgiebelartig zugespitzte doppelbrechende Platten aus heissem wasser. Schmp. 112° (unkarr.). Der Geruch ist stark ausgeprägt und erinnert etwas an ranzigen speck".

The melting point of these crystals, however, was found to be 90° rather than 112°. This value checks more closely with the 92° - 94° reported by Snyder, Kuch and Johnson. These investigators also reported that even the purest specimens of butane boronic acid did not show a sharp melting point when the temperature was raised at the rate of one degree per minute. They found that during the fusion a slow effervescence occurred, which became vigorous above 100° and that samples which had undergone
vigorous effervescence did not resolidify on cooling, but those which had been heated less strongly resolidified and melted again.

There is a lack of agreement in the composition, melting point, and derivatives of the aliphatic boronic acid due to the greater part of obtaining specimens of these acids, which actually correspond to the formula RB(OH)$_2$. The acids usually separate from the aqueous solutions as hydrates, and the latter on standing over the drying agent pass through the stage of the anhydrous acid RB(OH)$_2$ and finally yield alkyl boronoxides of the composition RBO. Furthermore, dry samples of the aliphatic boronic acids undergo atmospheric oxidation to give a product contaminated with H$_3$BO$_3$.

The reducing action of butane boronic acid on ammoniacal silver nitrate was verified but the 50% yields reported by Snyder, Kuch, and Johnson were not attained.

The method devised for the preparation of methyl borate worked very well and the yields of the crude product equal to 65% of the theoretical amount was very good.

The purification of methyl borate by washing with cold concentrated sulphuric acid appeared quite successful since the product burned with a bright green flame and boiled between 67° and 70° C, results which are in accord with those found by Seaman and Johnson. These investi-

William Seaman, John R. Johnson, op. cit., 714.
gators found that the diverse boiling points for methyl borate (55 to 72°C) reported in the literature are probably due to the fact that methyl borate forms an azeotropic mixture with methyl alcohol from which it is relatively difficult to remove the lost traces of alcohol. They reported the following properties for the methyl borate obtained after treatment with sulphuric acid: b.p. 67-67.8° at 75° mm., d₂₀ 0.932, n₂₄ 1.3558.

There are, of course, a large number of problems still remaining in the field of organo boron compounds. One of the most interesting of these is the possibility of preparing mixed trialkyl or triaryl borines or even a combination of the two. No one has as yet been successful in accomplishing this and very little work along these lines has been reported in the literature. Krause and Nitsche, Erich Krause, Rudolf Nitsche, op. cit., 2790.

found from their work that the existence of such compounds was highly probable. In an attempt to solve this problem, however, and to prepare diethyl, phenyl borine by the reaction of phenyl boron oxide with ethyl magnesium bromide, the vacuum distillation of the product yielded triethyl borine and an oil, triphenyl borine showing that a rearrangement had taken place.

It may be possible to develop a method for isolating the final product without distillation or the preparation may be carried out under different conditions using other
reagents which might not cause the rearrangement. It is possible, for example, that mixed compounds could be prepared by using reagents such as dimethoxy boron fluoride \((\text{CH}_3\text{O})_2\text{BF}\) or methoxy boron difluoride \(\text{CH}_3\text{OBF}_2\) and employing first the procedure for the preparation of butane boronic acid used in this experiment to introduce one alkyl radical; omitting the hydrolyses of the remaining groups on the boron atom; isolating the resulting compound; and then proceeding with the method used for the preparation of tri-n-butyl borine but employing a different alkyl or aryl radical in the Grignard reagent.
ANNOTATED BIBLIOGRAPHY

BOOKS


The book contains a group of forty-eight experiments illustrating preparations using the fundamental classes of organic reactions. Included are the preparation of anhydrous ether and the preparation of a Grignard reagent.


This is the classic book on inorganic chemistry listing most inorganic compounds, their reactions, and methods for their preparation. The original references for the various preparations of methyl borate are listed here.


This is the most comprehensive work on organic chemistry, listing and classifying as many organic compounds as possible along with their properties, reactions and methods for their preparation. Original references for some preparations of methyl borate are given here.


This book gives general notes on the preparation and action of Grignard's reagents along with various theories as to the constitution of Grignard's Reagents.
PERIODICALS


This article reports esterification of boric acid and methyl alcohol taking place at room temperature without the aid of a catalyst as determined by the spontaneous evaporation of boric acid in a methyl alcohol solution.


Triborine, triamine, dimethylamine and B$_2$NH$_7$ were studied by means of an electron diffraction experiment. The benzene like structure of the first of these was confirmed and the B-N distance determined. Structures and distance of other linkages were determined.


This article reports an electron diffraction investigation of the vapors of methyl borate and of trimethyl triborine trioxane. The electron configurations of these substances are discussed. The available data on structures of boron compounds is reviewed.


This article reports the preparation and characterization of two new compounds BH$_3$CO and (CH$_3$)$_3$NBH$_3$. The rate of decomposition of the former suggests that free molecules of borine, BH$_3$, may be involved in the process.

Various assumptions of active and inactive forms as well as other specific assumptions of the octet theory are used to interpret the properties of the double bond and are applied to various reactions characteristic of the double bond.


The preparation of trimethyl and triethyl borine by the interaction of zinc alkyls and ethyl borate is described as well as the preparation of ethane boronic acid by the slow oxidation and consequent hydrolysis of triethyl borine.


Internal polar properties of atoms and groups may be classified either according to time dependence or according to mechanism. The two classifications are not quite co-extensive and their interrelationship is considered. Anomalous examples of orientation, reaction, velocity and chemical equilibrium are considered from the point of view indicated.


The preparation of tri-n-butyl borine, its reaction with anhydrous HBr, aqueous HBr, anhydrous bromine, dealkalation, chlorination with t-butyl hypochlorite, and the electronic interpretation of these reactions is discussed.

The behavior of tri-n-butyl borine toward hydrogen peroxide, perbenzoic acid and molecular oxygen; the mechanism of the oxidation process and of the inhibiting action of water is discussed.


This paper reports the preparation of 2-furan and 2-thiopheneboronic acids and aliphatic boronic acids containing the benzyl and t-butyl groups. The first two are reported similar, the latter different in chemical action from the aromatic boronic acids. Atmospheric oxidation and the reduction of ammonical silver nitrate by these acids is discussed and it is suggested that the reduction involves the formation of an unstable silver alkyl.


This article offers the reaction of fused borax, HCl and the corresponding alcohol as a general method for the preparation of small amounts of boric esters in the laboratory without the aid of an autoclave.


This article reports the reactions of several organomagnesium compounds of the aromatic and aliphatic series with the various boric acid esters. The isobutyl ester is reported as easiest to
prepare and gives the best yields. The preparation and properties are given for tri-n-propyl borine, and phenyl benzyl, methyl, ethyl, propyl, and iso-butyl boronic acids.


It is reported that the organoboric acids studied do not associate in nitro-benzene and that in this solvent there is no appreciable amount of hydrogen bond formation contrary to previous theories.


In this article cyclic structures for the organoboron oxides are proposed in keeping with the double, triple and higher molecular weights found.


The properties of trialkyl borines and organo boron acids are given. The preparation of boron trifluoride and its use in the preparation of tri-iso-amyl borine, tri-iso-butyl borine, and tri-n-propyl borine is explained. The slow oxidation of trialkyl borines to the oxides and hydrolysis to the organo boron acids is described in connection with the preparation of iso-pentane boronic acid, iso-butane boronic acid and propane boronic acid.

This article reports the preparation of various trialkyl and triaryl borines and their reaction with the alkali metals. The possibility of the preparation of mixed trialkyl or triaryl or both is discussed.


These articles discuss the properties of the compounds in the camphene series, the possible mechanisms of the reactions and the rearrangement of one compound due to the presence of another. The effect of ionization and solvents on racemization and reaction velocity is discussed.


The order of the ease of transformation of camphene hydrate esters into iso-bornyl esters, other transformations and reaction mechanisms are discussed.


The preparation of camphor dichloride is reported. The different action of catalysts in different solvents is attributed to the dielectric constant of the solvents.


The preparation of monophenyl boron dichloride C₆H₅BCl₂ by the action of mercury diphenyl with BCl₃ is described as well as the preparation of several derivatives of this compound including phenyl boronic acid.

The electronic theory of organic reactions is summarized. Reagents are classified as electrophilic or nucleophilic.


The preparation of methyl borate by heating methyl alcohol and boric anhydride in an autoclave is described.


This article reports that the methyl derivatives of borine trimethylamine have been prepared and characterized. Borine dimethyl etherate and symmetrical dimethyldiborane were obtained and their structures established.


This article reports that the four ethyl derivatives of diborane and mono-n-Propyl-diborane and di-n-Propyl-diborane have been prepared and are analogous to corresponding methyl derivatives of diborane.


The preparation of mono, di, and tri-n-methyl derivatives and B-methyl derivatives of triborine triamine are described as a confirmation of the ring structure of triborine triamine.

In this article the preparation of four methyl derivatives of diborane is described. Their properties and constants have been determined and their reactions and structures studied.


Attempts made to devise new methods for the preparation of aromatic boronic acids and to improve the yields. The chemotherapeutic effects of derivatives of phenylboric acid were studied.


The importance of organoboron compounds in the development of electronic theories of organic reactions is explained. Procedures for the preparation and reactions of 1-butane boronic acid, 1-hexaboronic acid and others are given.


The article reports a study of the properties of tri-methyl borine and tri-ethyl borine and predicts C2H6 as the simplest hydride existing.


The more recent developments in the chemistry of boron hydrides and the structural problems connected with them are summarized. The compounds already prepared are listed and the original references given.

In this paper the unstable sextet theory of organic reactions is outlined and applied to intramolecular rearrangements.