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INVESTIGATION OF THE SYNTHESIS AND  
TESTING OF VARIOUS POSSIBLE BORON-ORGANO AND  
OTHER SIMILAR POLYMERS

L. E. STOUT  
D. F. CHAMBERLAIN

WASHINGTON UNIVERSITY

JUNE 1952

WRIGHT AIR DEVELOPMENT CENTER

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WADC TECHNICAL REPORT 52-192

**INVESTIGATION OF THE SYNTHESIS AND  
TESTING OF VARIOUS POSSIBLE BORON-ORGANO AND  
OTHER SIMILAR POLYMERS**

*L. E. Stout  
D. F. Chamberlain*

*Washington University*

*June 1952*

*Materials Laboratory  
Contract No. AF 33(038)-23299  
RDO No. 604-302*

**Wright Air Development Center  
Air Research and Development Command  
United States Air Force  
Wright-Patterson Air Force Base, Ohio**

## FOREWORD

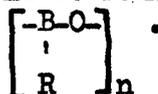
This is the final comprehensive report of a series prepared by Washington University, St. Louis, Missouri. Work at Washington University was initiated as a project by the Air Materiel Command under Air Force Contract No. W33(038)-23299 and Research and Development Order No. 604-302 entitled "Investigation of Boron-Organic Compounds." Administrative responsibility was subsequently transferred to the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Lt R. M. Luck acting as Project Engineer.

The personnel assigned to this project were: Dr. L. E. Stout, Dean, School of Engineering and Dr. D. F. Chamberlain, Professor of Chemical Engineering.

## ABSTRACT

Exploratory work on the preparation of organo-titanium and organo-boron compounds is described. Initial efforts were directed toward the synthesis of compounds of the type  $R_2Ti(OH)_2$  and  $RB(OH)_2$ . The work on titanium supports the evidence previously reported in the literature, that titanium-organocompounds, involving a Ti-C bond, cannot be formed.

Efforts to synthesize the boronic acids  $RB(OH)_2$  were moderately successful; of the alkyl derivatives, the propyl, butyl, and hexyl were isolated; of the aryl type, only the phenyl derivative was obtained. All proved to be heat and moisture sensitive, and no condition of temperature, concentration, time, atmosphere, or catalyst could be found which would induce condensation polymerization to



Organo complexes of boron trifluoride and dihydroxyfluoroboric acid were formed. Heating of these complexes produced various reactions, primarily decomposition, but did not result in polymer formation.

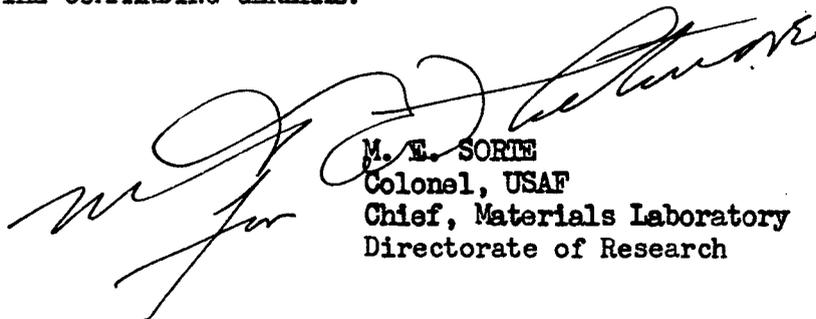
Condensation polymers were formed from boric acid and various glycols, but all were low melting and water soluble. Polymers were also formed from various mixtures of glycerol, boric acid, and phthalic anhydride (or maleic anhydride, or fumaric acid). Again the polymers were low melting and water sensitive.

It is concluded that the boronic acids do not undergo condensation polymerization similar to the dihydroxy silicones, but decompose to boric acid or the anhydride. Further, when polymeric esters or amides containing boron are formed, the presence of the boron introduces extreme water sensitivity.

## PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDING GENERAL:



M. E. SORIE  
Colonel, USAF  
Chief, Materials Laboratory  
Directorate of Research

## Table of Contents

I	Introduction .....	1
	Object of Project .....	1
	Summary of Literature .....	1
II	Discussion .....	8
III	Conclusion .....	22
IV	Bibliography .....	24
V	Appendix .....	26

## I. Introduction

### A. Object of Project

The object of this project was to prepare laboratory amounts of possible boron-organo and/or related polymers, and to make such mechanical, thermal, and chemical tests as were deemed necessary, and which could be performed with equipment on hand in the Chemical Engineering Laboratories.

The problem was purely exploratory, and in accordance with the terms of the contract, no samples of intermediates or polymers were furnished to the Wright Air Development Center.

The interest in boron and related polymers stems from the extremely useful properties which the various silicones have been found to possess. It was hoped that the substitution of other high melting elements in place of silicon might enhance these properties, particularly that of thermal stability.

Those elements which are suggested from a comparison of melting points include the following:

	<u>M Pt - °C</u>
Boron	2300
Iridium	2350
Molybdenum	2620
Platinum	1755
Tantalum	2850
Thorium	1845
Titanium	1800
Tungsten	3370
Vanadium	1710
Zirconium	1700

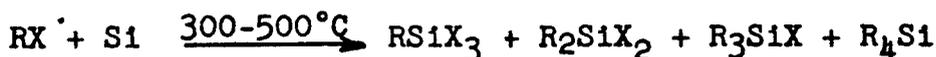
For various reasons (personnel available, cost and availability of chemicals, and the desirability of concentrating on one, or at the most, two materials) it was decided to investigate only boron and titanium.

### B. Summary of Literature Survey

#### 1. Methods of Producing Silicones

A survey of the material in Rochow, "Chemistry of the Silicones" (40) and in Post, "Silicones and Other Organic Silicon Compounds", (36) indicates that three general methods are available for preparing Si-C bonds.

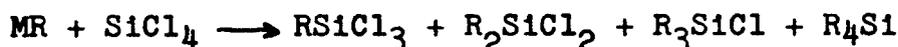
1. Silicon Metal plus Alkyl Halide



2. Grignard Reagent +  $SiCl_4$



3. Organometallic Compound +  $SiCl_4$



It is apparent that all methods lead to mixtures. Industrially, methods (1) and (2) appear to be practiced. In general, the most useful compounds are of the type  $R_2SiCl_2$ , which by hydrolysis and condensation, either simultaneously or in separate steps, can be converted into polymers of various forms, such as  $(R_2SiO)_x$ . These polymers differ considerably in properties and structure, but generally can be grouped as oils, resins, and elastomers. The oils are composed of linear molecules of finite length, the resins are cross-linked aggregates of cyclic and linear structures, and the elastomers are superpolymers of much higher molecular weight and of unknown configuration.

Because of the special interest of this project in the resins, additional material about this class is of value. In a strict sense, the methyl silicone resins are not silicones at all, because they require cross-linking in order to attain resinous properties, and hence the R/Si ratio is always less than two.

Three methods are available for preparing the cross-linked resins from the chlorides:

1) From dimethyldichlorosilane or its esters.

Hydrolyze compounds such as  $(CH_3)_2SiCl_2$ , then oxidize with air and a catalyst to attain the desired  $CH_3/Si$  ratio. (16)

2) From dimethyldichlorosilane mixed with monomethyltrichlorosilane or silicon tetrachloride. (39)

Hydrolyze a mixture of the desired proportions, and then condense the products.

3) From silicon tetrachloride.

Silicon tetrachloride may be partially methylated, as with methyl magnesium chloride, to the desired  $CH_3/Si$  ratio, and the product hydrolyzed and condensed directly.

The methyl derivative is of special interest because it alone of all possible derivatives contains no C-C bonds, and involves the fullest use of the inorganic character of the siloxane network.

Resins of  $\text{CH}_3/\text{Si}$  ratios of 1.0, 1.2, 1.3, 1.4, 1.5, and 1.7, among others, have been prepared. Below 1.2 methyl groups per silicon atom the resins are sticky syrups which cure at room temperature, or with moderate heating, to hard, brittle, glassy masses. Between 1.2 and 1.5 the polymers are colorless solids which harden at  $100^\circ\text{C}$  in 2 - 24 hours. Above 1.5, and particularly above 1.7, the products are oily, volatile, but set to a soft gel after 2-14 days at  $200^\circ\text{C}$ .

Other resins besides the methyl derivatives have been investigated. Substitution of ethyl for methyl yields compositions which are softer, more soluble, and slower to cure. The preferred range is 0.5 to 1.5 ethyl groups per silicon atom. At about a one to one ratio the products are suitable as coatings, having good adhesiveness and fair flexibility. Above 1.5 ethyl groups the silicones are difficult to condense, and above 2.0 the products are non-resinous oils.

Little is known of intermediate polymers of the higher alkyl compounds. The larger the group used, the slower is the resin to cure, and the softer it is. They also oxidize more readily, and crack and check easily.

The aryl derivatives, such as phenyl silicone, have properties distinctively different from those of the alkyl, especially methyl. Whereas hydrolysis of dimethyldichlorosilane yields immediately a wide assortment of polymers, and no compound such as  $(\text{CH}_3)_2\text{Si}(\text{OH})_2$  has ever been isolated, hydrolysis of  $(\text{C}_6\text{H}_5)_2\text{SiCl}_2$  yields an almost theoretical equivalent of diphenylsilanediol,  $(\text{C}_6\text{H}_5)_2\text{Si}(\text{OH})_2$ , which can be recrystallized and obtained in a pure form melting at  $148^\circ\text{C}$ . The diol, however, above  $30^\circ\text{C}$ , begins to condense, yielding linear polydiols, and cyclic trimers (in acid) and tetramers (in bases). At  $100^\circ\text{C}$ , the polydiols condense further, and at  $200^\circ\text{C}$ , condense rapidly to resins. The resins soften at elevated temperatures, are weak and brittle when cold, burn with a sooty flame, but are markedly resistant to oxidation. By chlorinating the nucleus, brittle, fusible resins are obtained, which are less flammable, but still weak.

Resins produced from other aryl compounds have similar properties, although phenoxyphenyl silicone produces a hard, brown, brittle resin of high thermal stability and good electrical properties.

To sum up the above, it can be said that alkyl silicone resins

are apt to be slow to form, and soft when produced, whereas aryl derivatives are brittle and weak. By producing copolymers, such as methyl-phenyl and ethyl-phenyl silicones, considerable improvement in strength is obtained without sacrifice of other desirable properties, and, therefore, the alkyl-aryl copolymers are more useful whenever strength and toughness are important. As an example, methyl-phenyl silicone, when the molar proportions of methyl and phenyl are almost equal, and the total R/Si ratio is about 1.8, has a very good balance of flexibility, strength, and infusibility (in the cured condition). Such resins, in the form of films cured on glass fiber cloth, have excellent dielectric strength and heat resistance.

## 2. Boron-Organic Derivatives

Relatively little useful information on boron-organic compounds appears in the literature. Frankland and Duppa,<sup>(14)</sup> in 1860, were the first to report the preparation of boron-organic compounds, using boron halides and zinc alkyls. In 1909, Khotensky and Melamed<sup>(19)</sup> described the preparation and some properties of methyl, ethyl, propyl, isobutyl, and isoamyl boronic acids from the Grignard. The methyl and ethyl derivatives are reported as difficult to secure in any yield because of their great volatility.

In 1921, Krause and Nitsche<sup>(25)</sup> reported the preparation of the mono alkylboronic acids by slow oxidation of the trialkyl derivatives. The same authors, in 1922<sup>(26)</sup>, reported on the preparation of aryl boronic acids.

In 1929, Pace<sup>(33)</sup> gave directions for preparing phenyl dichloroboron from benzene and  $\text{BCl}_3$ , in the presence of Pd black at 500-600°C.

In 1930, König and Scharrnbeck<sup>(21)</sup> reported the preparation of a considerable number of the higher alkyl and some aryl boronic acids, by means of the Grignard and  $\text{BCl}_3$ .

In 1931, Krause and Knobbe<sup>(24)</sup> reported the preparation by the Grignard reaction of tri-p-anisyl boron, tri-t-butyl boron, t-butyl boronic acid, and tri-sec-butyl boron.

In 1931, Seaman and Johnson<sup>(43)</sup>, and in 1932, Bean and Johnson<sup>(2)</sup>, used and extended the work previously reported by Khotensky and Melamed<sup>(19)</sup>.

Burg and Schlesinger<sup>(8)</sup> in 1933 reported the preparation of dimethoxy borine from boron hydride and methyl alcohol. Mal'nikoff<sup>(29)</sup>, in 1936, reported on the action of halogens and hydrogen peroxide on diaryl boronic acids. The aryl compounds were prepared by the Grignard reaction, using  $\text{BCl}_3$ , following the

methods of König and Scharrnbeck.

Krause, in 1937, in his "Die Chemie der Metall-organischen Verbindungen" (27) described the preparation of alkyl derivatives of the  $R_3B$  type, and of aryl derivatives of the  $RBX_2$  and  $RB(OH)_2$  types.

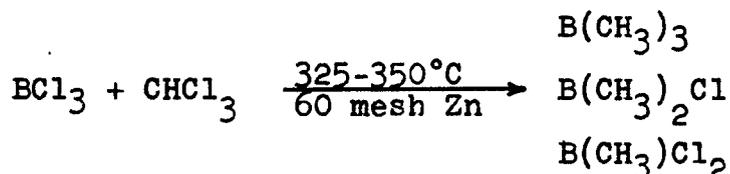
In 1938, Mel'nikov (30) discussed the rapid determination of boron in arylboronic acids.

In 1938 also, Mel'nikov and Rokitskaya (31) continued the work of König and Scharrnbeck, and prepared other aryl and diarylboronic acids from the corresponding Grignards.

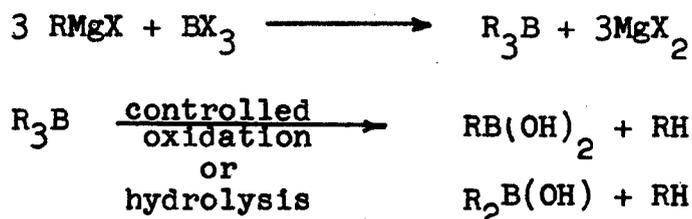
Walters and Miller (49), in 1946, described the analysis of  $BF_3$  dissolved in ether.

U.S. Patent 2,457,603 (1948) (48) describes the preparation of polyvinylborates, by reacting compounds of the type  $RB(OH)_2$  to form the polyvinyl ester. R here stands for aliphatic or aromatic groups, or their halogen, hydroxyl or amino-substituted derivatives.

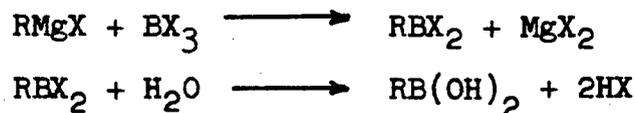
British Patent 618,358 (1949) (6), concerns the preparation of organo-boron compounds by the reaction:



The literature on boron-organo acid derivatives can be summed up by saying that compounds of the mono boronic acid type have been prepared by a rather hazardous procedure involving:

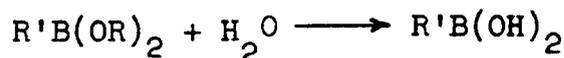
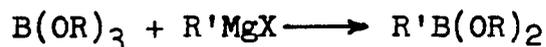


Contrasted to this, the aryl derivatives can apparently be made by a more direct procedure:



This more direct procedure has apparently not been successful in the preparation of the alkyl derivatives.

In addition, a third and more involved method of synthesis necessitates the formation of a tri ester of boric acid, followed by a reaction between the ester and a Grignard:



### 3. Titanium - Organo Derivatives

A review of the literature covering the formation of Ti-C bonds indicates that up to the present, despite considerable work in the field, no evidence of the formation of a stable Ti-C bond has been produced. Various methods of attack have been investigated, without success. Briefly, the articles pertaining to the formation of Ti-C bonds can be summarized as follows:

Cahours<sup>(9)</sup> in 1862 first attempted to react  $\text{TiCl}_4$  and  $\text{Zn}(\text{C}_2\text{H}_5)_2$ , and obtained nothing but a black reaction product.

Köhler<sup>(20)</sup> in 1880 reported attempts to react  $\phi\text{PCl}_2$  and  $\text{TiCl}_4$ , with no evident success.

In 1888 Schumann<sup>(42)</sup> reacted  $\text{Zn}(\text{C}_2\text{H}_5)_2$  and  $\text{TiCl}_4$  but obtained no ethyl titanium compounds.

In 1889 Petero and Peratoner<sup>(34)</sup> continued the work on  $\text{Zn}(\text{C}_2\text{H}_5)_2$  and  $\text{TiCl}_4$ , and identified an intermediate complex  $\text{TiCl}_4 \cdot 2(\text{C}_2\text{H}_5)_2\text{Zn}$ . This complex was vigorously destroyed by water, yielding a gas, zinc, and an oil. The oil yielded n-octane plus another fraction boiling around  $220^\circ\text{C}$ , and reported to contain titanium.

Levy<sup>(28)</sup>, in 1892, found that titanium metal did not react with  $\phi_2\text{Hg}$ ,  $\text{Zn}(\text{C}_2\text{H}_5)_2$ , or  $\text{Al}(\text{C}_2\text{H}_5)_3$ . At  $110^\circ\text{C}$   $\text{Hg}(\text{C}_2\text{H}_5)_2 + \text{TiCl}_4$  gave  $\text{Hg}(\text{C}_2\text{H}_5)\text{Cl}$  and  $\text{TiCl}_3$ . Above  $180^\circ\text{C}$ , titanium metal was formed.

Challenger and Pritchard<sup>(10)</sup> in 1924 attempted to react various Grignards with  $\text{TiCl}_4$ . A vigorous reaction occurred, yielding a black product, but no titanium-organo derivative could be isolated, only R-R compounds and  $\text{Ti}^{+++}$ .

In 1927 Browne and Reed<sup>(7)</sup> reacted  $\text{Pb}(\text{C}_2\text{H}_5)_4$  and  $\text{TiCl}_4$ , but only obtained  $\text{TiCl}_3$ .

Razuvaev and Bagdanov<sup>(37)</sup>, in 1933, studied the reaction of  $\Phi$  MgBr and  $TiCl_3$ , but obtained no organo-titanium compounds.

In 1938, Pletz<sup>(35)</sup> (Russian) claimed the formation of butyl-titanium compounds by the action of n-butyl lithium on tri-ethoxytitanium chloride.

In what has certainly been the most complete study to date, Jones<sup>(18)</sup> and Gilman and Jones<sup>(15)</sup> reported that in the reaction between RLi or RMgX and the halides of titanium, the first stage of the reaction is the formation of a complex, as  $TiCl_4 \cdot XRLi$ . This complex is usually thermally unstable, and also easily hydrolyzed, and during its decomposition, the titanium is reduced to a lower valence state (apparently even to  $Ti^0$ ), and R:R products such as diphenyl and ethane are produced. No evidence of a Ti-C bond was found, and the authors cast definite doubt on the results of Pletz<sup>(35)</sup> by demonstrating that the intermediate complex, with no Ti-C bond, gives the characteristic tests reported by Pletz.

It is of interest to note that Gilman and Jones, in discussing the complexes formed by the above reactions, do indicate that possibly Ti-C bonds do form in complexes with RLi or RMgX, but that such bonds then decompose readily, yielding the free metal.

To sum up the above, it can be said that, with the exception of two papers, no work has been reported which demonstrates the formation of a Ti-C bond, and that considerable doubt exists as to the accuracy of the results reported in the two papers in question.

Another, more fruitful line of investigation with regard to Ti-organo compounds has been the preparation of numerous ortho-titanate esters. Various investigators (12, 3, 17, 5, 47, 22, 23, 38, 44, 11, 45, 46, 32) have prepared these esters in good yield, usually by reaction of  $TiCl_4$  with an alcohol in the presence of a base (NaOH,  $NH_3$ , pyridine, etc). The esters so produced range from high boiling, viscous, clear-to-yellow oils, to white solids, are easily hydrolyzed, do not form resins upon heating, but have been used as a vehicle in some enamels, and to produce modified oils, films, and resins (47, 23, 38, 44), and heat protective coatings (22).

The structure of these modified resins appears to be in doubt, but almost certainly the complex products produced do not have a Ti-O-Ti-O(etc) basic structure, as in the silicones.

## II. Discussion

### A. Initial Plan of Investigation

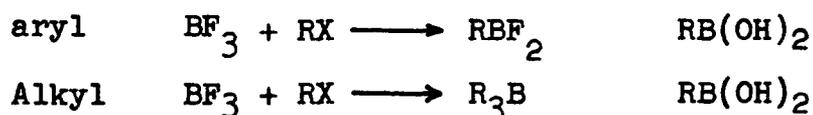
At the start, the work on this project attempted to follow the successful pattern established in the field of the silicones.

The literature survey on silicones indicates that the resinous type of silicone has a cross-linked structure in which the ratio or R/Si is less than 2, and the R is preferably a mixed aryl-alkyl type such as methyl-phenyl or ethyl-phenyl. This resinous material is formed by either oxidation of a material of substantially the composition  $(R_2SiO)_x$ , followed by further condensation, or by accomplishing simultaneous hydrolysis and condensation of mixtures such as  $R_2SiCl_2$  and  $RSiCl_3$  (or even  $SiCl_4$ ). In turn, the intermediate compounds needed, such as  $R_2SiCl_2$ , can be prepared by either of three methods: (1) by the Grignard, (2) from silicon metal plus an organic halide, (3) from organo-metallic compounds plus  $SiCl_4$ .

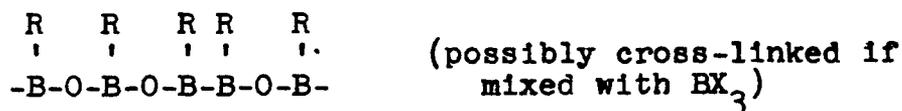
Based on the similarity to the silicone field, the compounds of initial interest were the boronic acids,  $RB(OH)_2$ , and the unknown titanium compounds,  $R_2Ti(OH)_2$ .

Our preliminary plan of attack can be summarized as follows:

1) To prepare boronic acids  $[RB(OH)_2]$ , through sequences such as:



2) To investigate the possible condensation of compounds of the type  $RB(OH)_2$  to form polymers of the general structure:



3) To prepare compounds of the type  $R_2Ti(OH)_2$ , by means unknown.

4) To investigate the possible condensation of compounds of the type  $R_2Ti(OH)_2$ , to form polymers of the general structure:



## B. Attempted Synthesis of Titanium Derivatives

In Experiments T-1 through T-26 (see Appendix for Experimental details) attempts were made to produce compounds of the type  $R_2Ti(OH)_2$ . The various methods used can be summarized as follows:

- 1) Conventional Grignard (Experiments T-1, T-2, T-3, T-5).

Use of ethyl and phenyl Grignards plus  $TiCl_4$ .

- 2) Modified Grignard (Experiments T-4, T-6, T-7, T-8, T-9, T-10, T-18, T-19).

Use of benzene or chlorobenzene as the solvent, with the phenyl Grignard and  $TiCl_4$ .

- 3) Reaction of titanium metal (Experiments T-11, T-12, T-13, T-14, T-15, T-16, T-17, T-20, T-21, T-22).

Attempts to react phenyl bromide in the vapor state with titanium metal, either alone or mixed with other metals such as copper, zinc, lead.

- 4) Wurtz-Fittig reaction (Experiments T-23, T-24).

Use of sodium metal plus phenyl chloride and  $TiCl_4$ .

- 5) Titanium nitride

Attempts to react  $TiN$  with benzene and phenyl chloride in the vapor state.

Of all these experiments, only type 2 resulted in any material which could possibly be a titanium-organo compound. In the last four of the experiments in this class (T-9, T-10, T-18, T-19), material was isolated from the benzene-soluble filtrate (which was obtained by filtering the reaction mass hot) which consistently analyzed 22-27% titanium. This material varied from a somewhat crystalline appearance, to stringy, gummy material. It was insoluble in organic solvents, hydrolyzed in water to give white  $Ti(OH)_4$ , and upon heating it turned gray and then black at about  $200^\circ C$ . After heating, the titanium content would be around 43%, which is very close to the theory amount of titanium in  $Ti(OH)_4$ , of 41.3%. The material also slowly decomposed on standing, with the titanium content gradually increasing.

No conclusive test was discovered by which the presence of a true titanium-carbon bond could be positively established.

Methods such as x-ray diffraction and spectroscopic analysis require a previously determined sample in order to calibrate the apparatus. If the compound were the desired titanium-organo material,  $\text{O}_2\text{Ti}(\text{OH})_2$ , it would analyze as follows:

Titanium	20.3%
Carbon	61.0
Hydrogen(available)	4.2

However, a sample of dried material, sent out for commercial analysis, was found to analyze as follows:

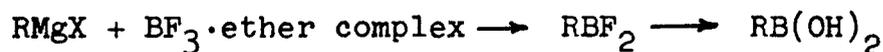
Titanium	27.5%
Carbon	18.4
Hydrogen(available)	4.4

Thus, the analytical evidence, plus the loss of organic material on standing, easy hydrolysis in water, and instability toward heat, all point to the existence of some complex, such as  $\text{Ti}(\text{OH})_4 \cdot x\text{C}_6\text{H}_6 \cdot y\text{H}_2\text{O}$ , rather than to an actual compound. The only real evidence supporting the existence of a compound is the ability to reproduce the titanium content readily when the material is freshly prepared, and the inability to change the titanium content by washing with other solvents in addition to benzene. However, the complex may be stable enough to resist such solvent action.

The net result of this work was merely to substantiate the information already in the literature, eg, that titanium-organo compounds, involving the formation of a stable Ti-C bond, cannot be prepared.

### C. Preliminary Experiments on Boron Derivatives

Initial experiments in the boron field were in the direction of forming both alkyl and aryl boronic acids by the more direct synthesis:



This was attempted in spite of literature evidence which indicated that the alkyl derivatives could not be prepared in this fashion. However, the hazards associated with the handling of the trialkyl boron compounds (spontaneously combustible upon exposure to oxygen), in the synthesis recommended, made it worthwhile to attempt the more direct reaction first.

In experiments B-1, B-3, B-8, B-9, and B-10, the preparation of phenyl boronic acid was attempted, by the method of Krause and Nitsche(26) which consists essentially of adding phenyl

Grignard in the cold to the  $\text{BF}_3$ -ether complex, followed by a two hour reflux and subsequent hydrolysis with ice water. A vigorous and apparently fairly complete Grignard reaction resulted, but all yields were low (18% and below, as indicated in Table I).

Table I

Exper.	$\text{BF}_3$ -ether complex	MgBr	Temp*	Reflux	Yield
B-1	0.33 gm moles	0.33 gm moles	0°C	1/2 hr	small
B-3	0.62	0.67	0	2	10.9
B-8	0.75	0.33	-80	0	small
B-9	0.75	0.33	-80	2	18.0
B-10	2.25	0.76	0	7	small
B-17	2.0	1.0	0	0	0**
B-18	2.5	1.0	0	0	0***

\* Temperature at the start of Grignard addition.

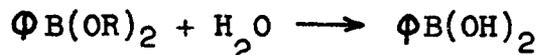
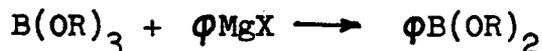
\*\* Various variations in the hydrolysis by means of water were tried, without success.

\*\*\* Various hydrolytic agents were tried, other than water, without success.

In Experiments B-4, B-5, B-6, and B-7, attempts similar to the above were made to produce ethyl and n-butyl boronic acids, using the sequence  $\text{RX} \rightarrow \text{RMgX} \rightarrow \text{RBF}_2 \rightarrow \text{RB(OH)}_2$ . No alkyl boronic acids could be isolated by this procedure.

Inasmuch as this method of Krause and Nitsche's had not worked well for either the aryl or alkyl derivatives, work on it was terminated.

In the aryl field, attention was focused on an ester method first reported by Khotensky and Melamed<sup>(19)</sup>, later improved by Seaman and Johnson<sup>(43)</sup>, and Bean and Johnson<sup>(2)</sup>.

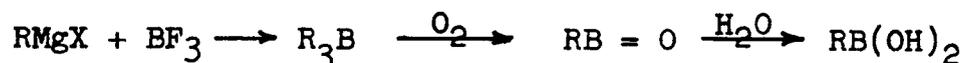


The ester used is preferably the n-butyl derivative, the

preparation of which is given in "Organic Synthesis"(1). By this procedure, a considerable quantity of  $(n-C_4H_9O)_3B$ , in 94% or better yield, was prepared.

Portions of the distilled ester were then reacted with the phenyl Grignard, followed by the operations of acid hydrolysis, alkaline steam distillation (to remove n-butanol), crystallization, filtration and drying. Yields varying from 10 to 35% of phenyl boronic acid, melting point 209-210°C (vs literature values of 204°C and 216°C), were obtained. The results of varying the batch size seemed to bear out literature information that as the batch size increased, the yield fell off.

During the same period that the preparation of phenyl boronic acid was being carried out via the ester method, considerable work was devoted to the preparation of the alkyl boronic acids, based on work by Krause and Nitsche(25), Runge(41), and Krause and von Grosse(27). As previously outlined in the literature survey, this method involved the preparation of the trialkyl borons, followed by their slow oxidation and hydrolysis to the boronic acids:



In the initial experiments on triethyl boron (B-11, B-12) it was found that special equipment had to be devised to synthesize the trialkyl compounds. Several fires and one minor explosion resulted before a satisfactory unit was constructed. In addition, although the product appeared, from various properties, to be the desired  $(C_2H_5)_3B$ , in good yields, the boiling points never agreed with literature data. Further investigation led us to conclude that the formation of rather stable complexes was responsible for the differences in boiling points.

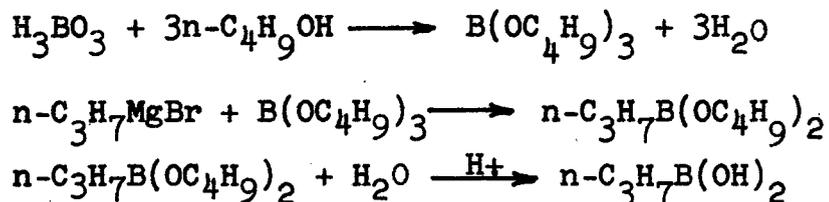
The literature information on the oxidation of the alkyl borons is rather indefinite, merely covering it by the use of "approximate methods". Results of our experiments (B-11, B-12, B-13, B-14, B-15, B-16) indicate that oxidation by various means (slow exposure of the concentrated material to air, bubbling air through dilute solutions, treatment of dilute solutions with hydrogen peroxide) results only in the formation of boric acid. In only one experiment (B-16) was any other significant material found, this being a small amount of white crystals mixed with a yellow oil. The crystals were found to melt at 37°C (vs literature data on ethyl boric acid of 40°C subl.).

In subsequent experiments (B-24, B-25) some work was carried out in an effort to form the tri-n-propyl boron, but no evidence was found to indicate that any was actually formed.

Because of the apparent difficulty in trying to oxidize triethyl boron, attempts were next made to synthesize the alkyl

boronic acids through the ester method used successfully for phenyl boronic acid. Based on admittedly inconclusive evidence obtained from the previous experiments, that the ethyl boronic acid, if formed, would be very unstable, it was decided to work on the higher homologs.

In Experiments B-26, B-27, and B-30, work on the propyl derivative was completed, involving the following sequence:



An 11% yield of a white crystalline product was the best obtained. The propyl boronic acid melted at 73-75°C (vs 74-75°C and 107°C in the literature).

The n-butyl boronic acid was prepared in Experiments B-31 and B-46. Only a small yield was obtained. It was found to be very difficult to separate the n-butyl boronic acid from the n-butanol formed in the reaction. After repeated recrystallizations, the material still melted low (88-93°C, vs 94°C in the literature).

The n-hexyl boronic acid was prepared in a 10% yield in Experiment B-53. The product was in the form of white crystals having a melting point of 86-88°C, vs 88-90°C in the literature.

Based on the idea that the first members of homologous series often have peculiar properties, attempts were made, in Experiments B-51 and B-52, to prepare methyl boronic acid by the ester method. A small amount of material was isolated in each case, which melted below room temperature, and which appeared to be very unstable. Results were inconclusive but not of sufficient interest to warrant further work.

As a last effort along this line, an attempt was made in Experiment B-60 to produce styryl boric acid  $[\text{C}_6\text{H}_5\text{CH}=\text{CHB}(\text{OH})_2]$ . It was felt that this material might be of some interest because of its possibilities toward both addition and condensation polymerization. The only organic product isolated was non-boron containing.

#### D. Stability Tests on Various Boronic Acids

In Experiments B-16, B-21, B-30, B-31, B-32, B-33, B-47, B-51, B-52, and B-69, data were accumulated on the stability of methyl, ethyl, n-propyl, n-butyl, n-hexyl and phenyl boronic acids.

These results can be summarized as follows:

1. Methyl Boronic Acid

The data in this case are rather inconclusive. If small yields of the methyl derivative were actually obtained, as the evidence seems to indicate, then the methyl boronic acid was very unstable and decomposed very rapidly in the presence of moisture.

2. Ethyl Boronic Acid

This material was also found to be quite unstable, and the small amount of material isolated, changed in a short time to boric acid.

3. n-Propyl Boronic Acid

The original material was in the form of small, rectangular white flakes, melting point 73-75°C. After five days storage in a desiccator, the material had changed to a yellow color, and in six days it was tan. Part of the material now appeared to melt at 80-90°C, part at 115-130°C, and part not at all. Decomposition had obviously occurred within a six day period, even in a dry atmosphere.

4. n-Butyl Boronic Acid

The original material was in the form of flat, colorless crystals, melting over the range 83-93°C. Repeated recrystallizations did not completely remove the last trace of n-butanol, which apparently was responsible for the low melting point.

When exposed to normal laboratory conditions for 23 days, the crystals were still largely in the form of butyl boronic acid. When held in an oven at 350°C, the butyl boronic acid completely decomposed in 20 hours or less (probably decomposed in a relatively few minutes). When held in a desiccator for 30 days, the crystals were about half decomposed.

5. n-Hexyl Boronic Acid

This material was in the form of white crystals which melted at 86-88°C. Temperature stability tests were run as follows:

<u>Temp.</u>	<u>Time</u>	<u>Results</u>
42°C	1 hr	Stable
62°C	1 hr	Partially decomposed
85°C	1 hr	Totally decomposed

The material was only slightly soluble in water, and for this reason was apparently more stable in the presence of water than were any of the other boronic acids tested.

At room temperature, in a desiccator, the hexyl boronic acid was stable for longer than 30 days.

## 6. Phenyl Boronic Acid

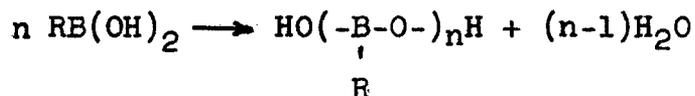
Phenyl boronic acid was isolated in the form of small white crystals. Melting points of various batches were usually 209-210°C, vs 204°C and 216°C in the literature. The acid was stable almost indefinitely in a desiccator, and for at least three months when exposed to laboratory air.

When held in an oven at 200°C, it decomposed in 4 hours or less, in both the normal atmosphere, and in the presence of dry nitrogen. It also decomposed in one-half hour or less in the presence of boiling water.

The results from stability tests generally indicated that only n-hexyl and phenyl boronic acids (of those tested) had sufficient stability to be of any interest as far as condensation polymerization was concerned.

### E. Attempted Condensation of Phenyl and n-Hexyl Boronic Acids.

In Experiments B-22, B-35, B-39, B-67A, B-68, B-73, and B-74, attempts were made to bring about a condensation polymerization:



In general, condensation polymerizations of this type are accomplished by using one of several methods; bulk, solution, or emulsion. To help in removing the usual small molecule formed (H<sub>2</sub>O, HCl, NH<sub>3</sub>, etc), aids such as the use of vacuum, heat, azeotropic distillation, bubbling of inert gas, and others, may be tried.

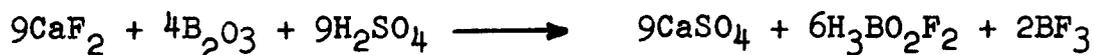
In the case of both phenyl and n-hexyl boronic acids, a number of such variations were attempted. In addition to simple heating of the solid acids, at normal atmosphere, under vacuum and in the presence of dry nitrogen, anhydrous solvents such as ether, benzene, and ethyl benzene were used, and also the condensations were attempted in the presence of dehydrating agents such as BCl<sub>3</sub>, BF<sub>3</sub>, and phosphorous oxychloride.

In no case was any evidence of a condensation type reaction observed. Simple heating, regardless of the atmosphere maintained, produced decomposition, and refluxing with an anhydrous solvent eventually resulted only in the isolation of the purified acid.

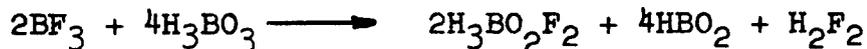
F. Work on Complexes of Boron Trifluoride and Dihydroxyfluoboric Acid.

Because of the ease with which boron derivatives form stable complexes with various organic compounds, it was decided to investigate the possible products produced by heating complexes of  $\text{BF}_3$  and of  $\text{H}_3\text{BO}_2\text{F}_2$ .

The necessary dihydroxyfluoboric acid ( $\text{H}_3\text{BO}_2\text{F}_2$ ) was prepared (B-43) in this laboratory, initially by the method<sup>2</sup> of Bowlus and Niewland<sup>(4)</sup>, involving this reaction:



The  $\text{BF}_3$  is then used again:



It was subsequently found that it was much simpler to produce the material by means of the second reaction only, using  $\text{BF}_3$  from a cylinder (B-44, B-61).

The following complexes were produced in the course of this work:

$\text{BF}_3 \cdot \text{ethanolamine}$	B-36
$\text{BF}_3 \cdot \text{aniline}$	B-42
$\text{BF}_3 \cdot \text{urea}$	B-54
$\text{H}_3\text{BO}_2\text{F}_2 \cdot \text{ether}$	B-45
$\text{H}_3\text{BO}_2\text{F}_2 \cdot \text{ethylene diamine}$	B-48
$\text{H}_3\text{BO}_2\text{F}_2 \cdot \text{urea}$	B-49
$\text{H}_3\text{BO}_2\text{F}_2 \cdot \text{triethylene glycol}$	B-62
$\text{H}_3\text{BO}_2\text{F}_2 \cdot \text{p-phenylene diamine}$	B-63, B-64, B-65

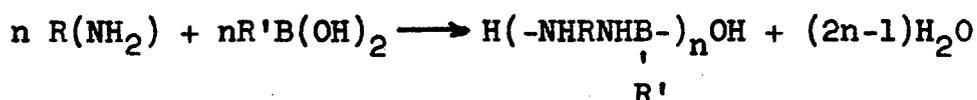
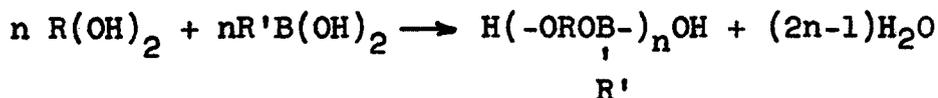
The complexes formed readily in all cases, except  $\text{H}_3\text{BO}_2\text{F}_2 \cdot \text{ether}$ , mostly as solids, off-white to tan in color. Heating of

the complexes produced either organic decomposition, with formation of carbon, or a water soluble melt. In most cases the melt appeared to be impure  $B_2O_3$ . In no experiment was any polymer of value obtained.

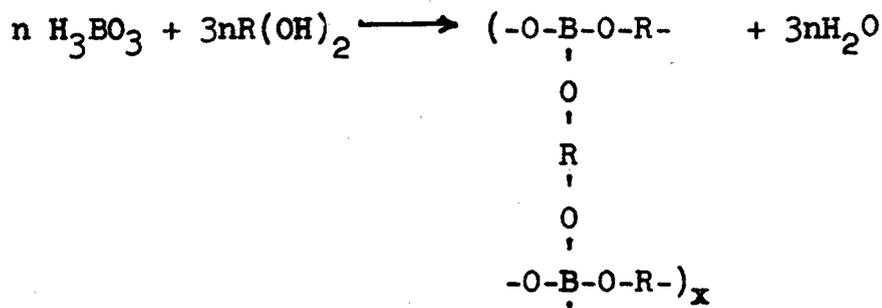
### G. Synthesis of Polymeric Esters or Amides

A considerable amount of work was carried out in this field, divided into three main divisions:

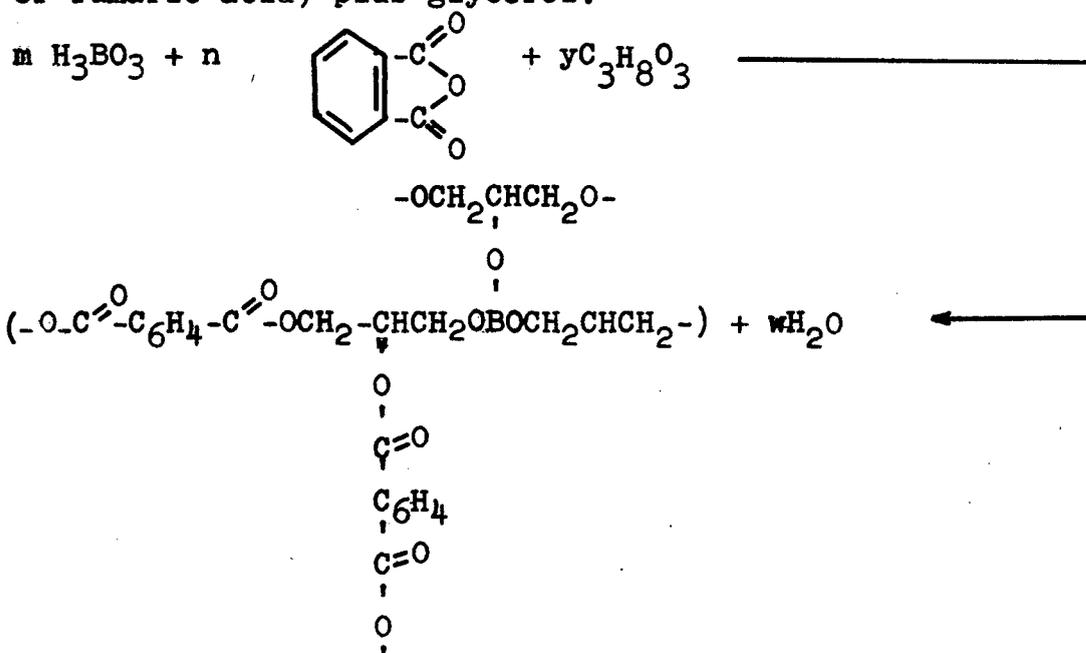
#### 1) Phenyl boronic acid plus glycols or diamines



#### 2) Boric acid plus glycols or diamines (B-34)



#### 3) Boric acid plus phthalic anhydride (or maleic anhydride or fumaric acid) plus glycerol.



In Experiments B-34, B-71, and B-72, attempts were made to condense phenyl boronic acid with ethylene diamine, propylene glycol, and m and p-phenylene diamines. Only in the reaction with m-phenylene diamine did any polymeric material form, and the products from all reactions were at least partially soluble in cold water, and completely soluble in hot water.

In Experiments B-37, B-38, B-55, B-56, B-57, B-58, B-59, B-70, and B-75, reactions involving boric acid and ethanalamine, ethylene diamine, glycerol, octylene glycol, polyethylene glycols (200, 300, 400), and p-phenylene diamine, were carried out. The boric acid plus ethanalamine and ethylene diamine gave water soluble, viscous liquids. With glycerol a clear polymeric resin was obtained from which, when molten, long, transparent, glass-like fibers could be pulled. The fibers slowly adsorbed moisture from the air, and became milky-white and wax-like, but still remained strong. However, samples of the melt were all water soluble, and prolonged heating did not reduce this water solubility.

Boric acid plus octylene glycol formed only a mobile liquid. Polyethylene glycol 200 gave a water soluble, semi-solid resin, from which fibers could be pulled. Polyethylene glycol 300 and 400 yielded viscous liquids. From p-phenylene diamine, a solid was obtained, but it was water soluble and non-resinous.

In the above reactions, both bulk and solution type of condensations were attempted, in order to get a greater extent of reaction. Even the use of dry nitrogen and an "azeotroper" tube (for separation of water formed) did not aid in producing better products.

In the work on the systems phthalic anhydride-boric acid-glycerol, fumaric acid-boric acid-glycerol, and maleic anhydride-boric acid-glycerol, the variables which were investigated included: ratio of boric acid to organic anhydride or acid, ratio of total acid or anhydride to glycerol, time, temperature, solvent, and use of an "azeotroper" tube.

The phthalic anhydride reaction gave resinous products from which strong fibers could be pulled. It was also found that various samples would bond plywood sections together very strongly. However, all samples would slowly adsorb moisture from the air, and turn milky white. The fibers lost their strength and the plywood sections would easily come apart. Some samples of the resins were not very soluble in cold water, but all were soluble in hot. Despite the fact that with the presence of both glycerol and boric acid, a cross-linked or thermosetting resin appears possible, and reactants were used in ratios such as to permit this, no amount of heating in a press at elevated temperatures caused thermosetting properties to appear.

The fumaric acid reaction also gave resins which were not particularly soluble in cold water, but which were completely soluble in hot. The maleic derivatives were all soluble in cold water.

The evidence from these experiments seems to indicate conclusively that the introduction of boric acid into the above systems, in any significant amount, brings about distinct water sensitivity in the resulting resin.

#### H. Work Based on the Results of Rollier

Professor Mario A. Rollier of the Institute of General and Analytical Chemistry, Polytechnic School, Milan, Italy, had been scheduled to present a paper on boron polymers at the XIIth International Congress of Pure and Applied Chemistry, in New York, September, 1951. Circumstances prevented his attendance and the paper was never given. However, when contacted, Professor Rollier released a copy of his proposed address.

Rollier had investigated three reactions: the preparation of dibutoxyphenylborine, the reaction of phenyl Grignard with  $\text{BCl}_3$ , and the reaction of a mixture of dibutoxyphenylborine and ethoxyboron dichloride with phenyl Grignard. The only part of the paper which was of particular interest with respect to boron polymers was in the discussion of the second reaction. Rollier claims that after hydrolysis of the reaction product, he obtained a very small yield of a boron-containing, semi-solid, oily paste which was stable even after prolonged contact with water. The yield, however, was reported to be so low as to prevent further study or analysis of the material.

In Experiments B-76 and B-90, Rollier's work on the second reaction was duplicated as closely as possible. Phenyl Grignard was added slowly to a  $\text{BCl}_3$ -ether solution, using a dry ice-acetone bath. The reaction mass was heated to drive off ether and excess  $\text{BCl}_3$  and  $\phi\text{Br}$ , and the resulting solid product was ground and reacted with water. In Experiment B-76, no reaction occurred until the water had been heated. In Experiment B-90, a reaction took place in the cold. The resulting solutions were extracted with ether, filtered, concentrated by evaporation, and distilled.

Distillation results are given in Table II, and compared with the data furnished by Rollier.

Table II

Comparison of Distillation Results  
With Those Reported by Rollier

Fraction 1

	<u>Temp and Press</u>	<u>Description</u>
Rollier	40-80°C/20-25 mm	Colorless liquid
Observed Exp B-76	35-50°C/0.7 mm	Colorless viscous liquid
Exp B-90	35-50°C/0.7 mm	Colorless viscous liquid

Intermediate Fraction

Rollier	- - - - -	- - - - -
Observed Exp B-76	- - - - -	- - - - -
Exp B-90	50°C/0.7 mm	White, gelatinous

Fraction 2

Rollier	80-105°C/15 mm	Yellow liquid
Observed Exp B-76	50-67°C/0.7 mm	Yellow liquid
Exp B-90	50-69°C/0.7 mm	Yellow liquid

Fraction 3

Rollier	130-175°C/15 mm	Yellow-pink vapor, yellow-brown gelatinous liquid
Observed Exp B-76	- - - - -	- - - - -
Exp B-90	- - - - -	- - - - -

None of the material obtained in fractions 1 and 2, and in the intermediate fraction, were found to contain boron.

In addition to the distillation fractions, a considerable quantity of dark brown still residue was left. Attempts were made to isolate compounds from this by various means (extraction, chromatographic adsorption, vacuum sublimation) but the only boron-containing material isolated was identified as phenyl boronic acid.

To sum up the results, it can be said that Rollier reported isolating a very small amount, Fraction 3, of a yellow-brown gelatinous liquid, boron-containing and stable to water. The results of Experiments B-76, and B-90, do not confirm this. In Experiment B-90, a fair quantity of a white, gelatinous material was isolated, stable to water, but non-boron containing.

A second part of Rollier's work was also investigated, to an extent further than he had reported. In Experiments B-88, B-89, B-91, B-92, and B-93, ethoxyboron dichloride was prepared by treating anhydrous ether with  $\text{BCl}_3$ , followed by fractionation, and the ethoxyboron dichloride reacted in turn with p-phenylene diamine or ethylene diamine. In the case of the ethylene diamine, the reaction was very violent, but the product isolated, although it contained boron, was non-polymeric and was water soluble. In the case of p-phenylene diamine, the product seemed to be mainly boric acid plus unreacted p-phenylene diamine.

### III. Conclusions

1. Synthesis of titanium-organo compounds containing a Ti-C bond was attempted, without success. Methods used included conventional and modified Grignards, reactions with titanium metal, a modified Wurtz-Fittig reaction, and reactions with titanium nitride. These results support literature data to the effect that such compounds cannot be formed.

2. A number of alkyl boronic acids were synthesized and some of their properties determined. The methyl and ethyl derivatives were obtained only in very small yields, whereas the n-propyl, n-butyl, and n-hexyl were obtained in yields of 10% or better. The phenyl boronic acid was also prepared in yields from 10 to 35%.

From stability tests it was decided that only the n-hexyl and phenyl boronic acids, of those tested, had sufficient stability to warrant attempts to condense them.

3. Attempts to bring about a condensation polymerization of phenyl and n-hexyl boronic acids, by various means, were unsuccessful. Both bulk and solution methods were tried and also the use of dehydrating agents and bubbling of an inert, dry gas was attempted. If conditions were too extreme, the acids were found to decompose; otherwise, the acids remained unchanged.

4. Complexes of boron trifluoride with ethanolamine, aniline, and urea, and complexes of dihydroxyfluoboric acid ( $H_3BO_2F_2$ ) with ether, ethylene diamine, urea, triethylene glycol, and p-phenylenediamine were prepared. Heating of these complexes produced either decomposition, with the formation of carbon, or a non-polymeric water soluble melt.

5. Polymeric esters and amides, containing boron, were prepared from phenyl boronic acid, boric acid, and boric acid-phthalic anhydride (or maleic anhydride or fumaric acid) mixes.

In the reaction with phenyl boronic acid, only m-phenylene diamine gave any polymeric material. The degree of polymerization of the polymer appeared very low, and it was water-soluble.

A number of polymers were prepared from boric acid, using ethanolamine, ethylene diamine, glycerol, octylene glycol, polyethylene glycols (200, 300, 400) and p-phenylene diamine. Many of the products were in the form of viscous liquids, but glycerol and polyethylene glycol 200 gave clear resins from which fibers could be pulled. However, the fibers adsorbed moisture very readily, turning white in the process, and the resins were all water soluble.

Similar results were found in producing resins from the systems: glycerol-boric acid-phthalic anhydride, glycerol-boric acid-maleic anhydride, glycerol-boric acid-fumaric acid.

Some of the resins had excellent appearance, and gave strong fibers. Some also bonded plywood firmly together. All resins produced, however, were water soluble, and adsorbed moisture readily from the air.

It is to be concluded from the results obtained in this series, that the introduction of any significant amount of boric acid in a resin system, resulting in the formation of polymeric boron-containing esters or amides, imparts extreme water sensitivity to the resulting resins.

6. The results reported by Professor Rollier of Italy, on the production in small yields, of a boron-containing, water-insensitive paste, as a result of the reaction between phenyl Grignard and boron trichloride, could not be substantiated. The only material produced that answered the description of his product, was found to contain no boron.

7. Reactions of ethoxyboron dichloride and diamines produced no polymeric material, and the products were all water soluble.

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## V. Appendix

Summary of Completed Experimental Work. Additional details of each experiment are given in the monthly reports AF 33(038) 23299-1 through AF 33(038)23299-11.

### A. Titanium

#### Experiment T-1

This experiment involved a conventional Grignard reaction, using  $C_2H_5MgBr$  and  $TiCl_4$ , in an attempt to form  $(C_2H_5)_2TiCl_2$ , and, by subsequent hydrolysis,  $(C_2H_5)_2Ti(OH)_2$ . A vigorous reaction resulted, yielding a viscous mass and finally a solid black reaction product. No organo-titanium compound could be isolated.

#### Experiment T-2

Experiment T-1 was repeated using an ice-salt bath in an attempt to hold the temperature at  $-15^\circ C$ . This attempt failed, however, because the reaction actually took place at the boiling point of ether, localized at the spot where the ether dripped in.

#### Experiment T-3

This experiment involved a Grignard reaction of  $\phi MgBr$  and  $Ti(OC_2H_5)_4$  (ethyl ortho titanate). A yellow-orange solid, melting over the range  $45-50^\circ C$ , was finally isolated from the black reaction mass, but it gave no test for titanium.

#### Experiment T-4

This was a modified Grignard in which chlorobenzene was used both as solvent and Grignard agent, to react with  $TiCl_4$ . Again, a black reaction mass was obtained, which was hydrolyzed with dilute  $HCl$  and extracted with various solvents, but yielded no titanium organo compound.

#### Experiment T-5

This experiment was a modified Grignard involving  $\phi MgBr$  and  $(n-C_4H_9O)_2TiCl_2$ . The half-ester was prepared by reacting anhydrous  $n-C_4H_9OH$  with  $TiCl_4$ . After completion of the Grignard reaction, followed by hydrolysis and extraction, no organo-titanium compound could be isolated.

#### Experiment T-6

This was a modified Grignard, using  $\phi MgBr$  and  $TiCl_4$  as the reactants, and benzene as the solvent. Again no organo-titanium compound could be isolated.

#### Experiment T-7

This was similar to Experiment T-6, but no hydrolysis

was carried out. The reaction mass was separated by vacuum distillation. The products identified in the distillate included phenyl bromide, diphenyl, and p-diphenyl benzene. The still residue gave a test for titanium, but a sample recrystallized from benzene contained only 0.18% Ti.

#### Experiment T-8

This was similar to Experiment T-6, with no hydrolysis; however, toluene was used as the solvent. No organo-titanium compound could be isolated.

#### Experiment T-9

This was similar to Experiment T-8, but the unhydrolyzed reaction mass was filtered hot, and washed with hot benzene. A small amount (about 0.5 gm) of red-brown material, grease-like in consistency, was obtained, which proved to be organic, and contained 22.2% Ti.

#### Experiment T-10

This experiment was a repeat of Experiment T-9. Again a greasy, brownish material was isolated from the benzene solution, and found to contain 21.5% Ti. After isolation it was found to have become insoluble in benzene. It was readily hydrolyzed in water, yielding a white flocculent precipitate and a yellow oil.

#### Experiments T-11, T-12, T-13, T-14, T-15, T-16, T-17

This sequence of experiments involved attempts to react titanium metal (or related material) with organic halides. The organic halide was fed slowly, in an atmosphere of helium, into a furnace, where it vaporized and passed over powdered titanium. The products and excess reactants passed out, condensed to liquids or solidified, and were separated from the helium.

It was felt necessary to use helium, or some other equally inert gas, because titanium reacts with both oxygen and nitrogen at temperatures above 150°C.

The titanium used was CP material, obtained in the form of various sized lumps from Fisher Scientific Co. It proved to be very hard, and could not be crushed in a steel roll mill, but was finally broken in a small jaw mill. The product was then screened through a U.S. Standard 14 mesh sieve, the oversize was recrushed, and the material that passed through was used in the experiments.

A review of the silicone literature, covering reactions between silicon metal and organic halides, reveals that various methods have been used to bring about the desired reaction:

- a) Si pulverized to 350 mesh, plus organic halide at 285°C.

b) Alloy of 50% Cu-50% Si, in chip form, plus organic halide at 312°C.

c) Powdered Si mixed with powdered  $\text{Cu}_2\text{Cl}_2$ , and the mixture heated to 265°C, gives a rapid reaction with evolution of  $\text{SiCl}_4$ , and the formation of reduced Cu deposited on the Si. This mixture is then reacted with the halide at 300°C.

d) Mixtures of Cu and Si powder are sintered together in a hydrogen atmosphere below the melting point of Cu. The sintered mixture was then reacted with the halide at 300-325°C.

e) Mixtures similar to (d) but containing Si and Ag, or Si and Zn.

These methods were taken as guides in our experimental work with titanium metal.

In Experiment T-11, bromobenzene was passed over 14 mesh (or finer) titanium, for 30 minutes, at 300°C. Some decomposition of bromobenzene occurred; no titanium-organo compound was obtained.

In Experiment T-12, the reactants were the same, the time was 70 minutes and the temperature was 500°C. Considerable decomposition occurred, some carbon was deposited in the reaction tube. No organo-titanium compound was isolated.

In Experiment T-13, the reactants were bromobenzene plus a mixture of 14 mesh titanium and copper powder. The temperature was 350 °C(?), the time 3 hours, 25 minutes. Again no titanium derivative could be isolated.

Experiment T-14 was similar to Experiment T-13, except that zinc dust was used in place of copper powder. The temperature was 350°C, the time 4 hours, 15 minutes. No titanium derivative was found.

Experiment T-15 duplicated Experiment T-13, but used lead powder in place of zinc. Again no titanium derivative could be found.

In Experiment T-16, powdered titanium was first mixed with cuprous chloride, and the mass heated to 280°C, in an atmosphere of helium. A vigorous reaction occurred, and a gas (either  $\text{TiCl}_4$  or  $\text{TiCl}_3$ ) was evolved. Bromobenzene was then passed over the titanium-copper catalyst for 2 hours, 40 minutes at 350°C. Again no organo-titanium material was isolated from the reaction products.

Experiment T-17 repeated the conditions of Experiment T-16, except that the temperature was kept at 400°C. No titanium-organo compound could be isolated.

#### Experiment T-18

This was a continuation of the work on Grignard reactions, using  $\phi\text{MgBr}$  and  $\text{TiCl}_4$ , with benzene as a solvent. Again a brownish, rather gummy solid was isolated from the benzene

solution. It was found that large amounts of this material could be produced by bubbling air into the benzene solution, and that once formed, it would not redissolve in the benzene solution. A sample of the material was dried at 100°C for one hour, and appeared to be somewhat crystalline under the microscope. Upon heating, it turned gray at 200°C, but even at 300°C it did not melt.

A sample of the material, after drying for one hour at 100°C, analyzed 26.7% Ti. A sample dried overnight at 40°C, analyzed 24.3% Ti. After drying for an additional two hours at 120°C, it analyzed 37.4% Ti.

A mixture of dry benzene and titanium tetrachloride was treated with a little water, yielding a gummy material somewhat similar to the above. Upon drying, it turned white, and was found to contain 27.2% Ti.

#### Experiment T-19

This experiment was a continuation of the Grignard type reaction, using benzene as the solvent. To avoid an excess of titanium tetrachloride, only half of the usual amount was used. This time, no gummy material formed after the hot filtration of the benzene solution. Only diphenyl could be isolated from the filtrate. The residue contained titanium, but not in the form of a titanium-organo complex or compound.

#### Experiments T-20, T-21

In these experiments, titanium powder was first sintered with copper powder at 400 and 800°C, and then the reaction with bromobenzene in the vapor state was attempted. No organo-titanium material formed.

#### Experiment T-22

This experiment involved a reaction of titanium material and cuprous chloride at 325°C, followed by an attempted reaction with bromobenzene at 400°C. Again no organo-titanium material formed.

#### Experiment T-23

This was an attempt to apply the Wurtz-Fittig reaction to titanium:



The sodium metal was added to the solvent, isopropyl ether, and to this mixture was added dropwise a mixture of  $\text{C}_6\text{H}_5\text{Cl}$  and  $\text{TiCl}_4$ . Then ethyl acetate was added, and the mixture refluxed for 18 hours. At the end of this time the solution had turned a deep brown color, but most of the sodium was unreacted. The

excess sodium was removed by filtration. A portion of the filtrate was evaporated to dryness, yielding two different types of material, one in the form of long, colorless needles, the other brown-black and amorphous. Both left a white ash when heated, but neither gave a conclusive test for organic material. There was no trace in the filtrate of any solid organic material, not even diphenyl.

#### Experiment T-24

Conditions of Experiment T-23 were repeated exactly, except that the reflux was continued for four days, and then the batch was allowed to stand at room temperature for an additional 5 days. The results were still in the negative.

#### Experiment T-25

This experiment was an attempt to form a titanium-organo compound, through intermediate formation of titanium nitride, TiN. Dry nitrogen was passed over titanium metal for one hour at 800°C. A copper-brown solid resulted, which was then treated with benzene vapor for 2 hours, 45 minutes, at 400°C. No evidence of any reaction was observed.

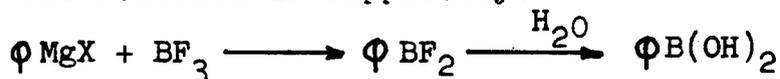
#### Experiment T-26

Conditions of experiment T-25 were repeated, except that the benzene was replaced by phenyl bromide. Again no evidence of reaction was obtained.

### B. Boron

#### Experiments B-1, B-3, B-8, B-9, B-10, B-17, B-18

These experiments were undertaken in an effort to prepare phenyl boronic acid, using the general method described by Krause and Nitsche<sup>(26)</sup>, which consists essentially of adding phenyl Grignard in the cold to the BF<sub>3</sub>·ether complex, followed by a 2 hour reflux and subsequent hydrolysis with ice water. The course of the reaction is supposedly:



Although small amounts of phenyl boronic acid were obtained, results in general indicated that during the hydrolysis step, most of the material was converted to boric acid. The use of other hydrolytic reactants, such as methyl alcohol, iso-butyl alcohol, 2-ethyl hexanol, 2-heptanol, and ethylene glycol did not improve yields. This method was, therefore, abandoned for one based on work by Khotensky and Melamed<sup>(19)</sup>.

#### Experiments B-4, B-5, B-6, B-7

These experiments were directed toward preparing alkyl derivatives (ethyl, n-butyl), of the form RB(OH)<sub>2</sub>, from

the hydrolysis of compounds of the type  $\text{RBF}_2$ . These attempts were made in spite of literature evidence that the proper method was to prepare compounds of the form  $\text{R}_2\text{B}$ , and then slowly oxidize them to  $\text{RB}(\text{OH})_2$ . The reason for doing<sup>3</sup>this was to avoid handling the spontaneously combustible  $\text{R}_3\text{B}$  material. All experiments, however, ended with the formation of  $\text{B}(\text{OH})_3$ .

Experiments B-11, B-12, B-13, B-14, B-15, B-16

These experiments were based on the work of Krause and Nitsche<sup>(25)</sup>, Runge<sup>(41)</sup>, and Krause and von Grosse<sup>(27)</sup>, for preparing  $\text{RB}(\text{OH})_2$  by the slow oxidation of  $\text{R}_3\text{B}$ , giving a sequence as follows:

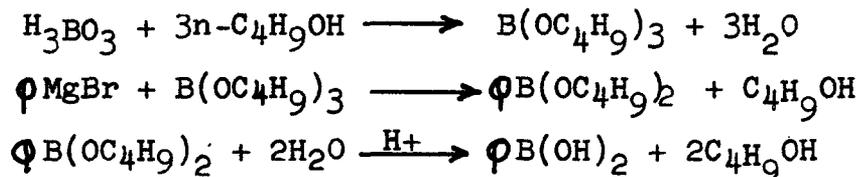


The equipment devised for carrying out the reaction and subsequent distillation to form the  $\text{R}_3\text{B}$  compounds from  $\text{RMgX}$  and  $\text{BF}_3$ ·ether complex was described in report AF 33(038)23299-2.

Results of these experiments indicate that triethyl boron was prepared; but that oxidation by various means (slow exposure of the concentrated material to air, bubbling air through a dilute solution, treatment of a dilute solution with hydrogen peroxide) resulted only in the formation of boric acid. In only one experiment (B-16) was any other significant material obtained, this being a small amount of white crystals, mixed with a yellow oil. The crystals were found to melt at  $37^\circ\text{C}$  (vs literature data on ethyl boronic acid of  $40^\circ\text{C}$  subl.). Because of the apparent instability of ethyl boronic acid, work on it was terminated.

Experiments B-19, B-20

These experiments were based on the work of Khotensky and Melamed<sup>(19)</sup>, using a boric ester instead of the  $\text{BF}_3$ ·ether complex as the source of boron, for the preparation of phenyl boronic acid by the following sequence:



The tri-n-butyl borate was prepared in 94% yield, with a boiling point of  $95\text{-}96^\circ\text{C}/0.7$  mm. This ester was then reacted with phenyl Grignard, the batch hydrolyzed with dilute  $\text{H}_2\text{SO}_4$ , made alkaline, the n-butanol steam distilled off, and several crops of crystals obtained from the residual liquor. The crystals were white needles which melted at  $204\text{-}208^\circ\text{C}$ , and after a week in the desiccator, at  $209\text{-}210^\circ\text{C}$  (literature data for phenyl boronic acid conflicting,  $204^\circ\text{C}$  and  $216^\circ\text{C}$ ).

#### Experiment B-21

This experiment was undertaken to test the stability of phenyl boronic acid. The evidence indicates that phenyl boronic acid is stable for at least three months at room temperature, but decomposes in four hours or less at 150°C, and in a half hour or less in boiling water.

#### Experiment B-22

This was the initial polymerization experiment, using a mixture of phenyl boronic acid and  $\text{BF}_3 \cdot \text{ether}$  complex, plus a small amount of  $\text{H}_2\text{SO}_4$  as a catalyst. A half solid-half liquid was formed, which tested for both boron and carbon. The material had no polymeric properties.

#### Experiment B-23

This was an attempt to prepare ethyl boronic acid, by the ester method used for phenyl boronic acid. Instead of tri-n-butyl borate, the methyl ester was used. No ethyl boronic acid was formed.

#### Experiments B-24, B-25

These experiments were carried out in an effort to form n-propyl boronic acid, through oxidation of the intermediate  $(n\text{-C}_3\text{H}_7)_3\text{B}$ . However, no evidence was found to indicate that any tripropyl boron had been made.

#### Experiments B-26, B-27

These experiments were carried out in an effort to form n-propyl boronic acid, using the ester method, with the triethyl ester as the starting material. However, no ethyl borate could be produced by the method used for n-butyl borate.

#### Experiment B-28

Several modifications in the preparation of tri-n-butyl borate were attempted, in order to shorten the method, without success.

#### Experiment B-29

This was an attempt to prepare a larger amount of phenyl boronic acid, for use in further polymerization experiments, and for possible shipment to Wright Air Development Center. However, as predicted in the literature, an increased batch size resulted in a decreased yield, and only 26.1 gm, or about 8% of theory was obtained.

#### Experiment B-30

This experiment was an attempt to prepare n-propyl boronic acid by the ester method, using the n-propyl Grignard and n-butyl borate. A 11.9% yield of small, rectangular white flakes was obtained, which melted at 73-75°C, vs 74-75°C in the literature.

The original white crystals, after five days in the desiccator,

changed to a yellow color, and in six days were tan. Melting point data were now rather indefinite, part of the material appearing to melt at 80-90°C, part at 115-130°C, and part not at all. Certainly the material had definitely changed its characteristics during the six day period.

Literature data on the melting point of propyl boric acid are not conclusive, Khotensky and Melamed(19) report 74-75°C, Krause and von Grosse(27) give 107°C.

#### Experiment B-31

This experiment was an attempt to prepare n-butyl boronic acid by the ester method. A small yield of flat, colorless transparent crystals was obtained; however, the crystals did not melt sharply, but over the range of 72-85°C, compared to literature data of 94°C and 104°C. The crystals appeared to be wet with n-butanol; a small amount was recrystallized from ether, yielding a material melting at 89°C.

A sample of the original crystals, exposed to laboratory conditions for 14 days, still contained some butyl boronic acid, but some  $H_3BO_3$  had also formed. Some solubility data were determined and reported.

#### Experiment B-32

This experiment involved a pilot plant production of n-butyl borate. The unit used included a 20 gallon stainless steel, agitated, jacketed kettle, reflux condenser, receiver, and vacuum system. The procedure followed was essentially that given in Report AF 33(038)23299-4, Experiment B-20. A good yield of a technical grade product was obtained, which was filtered and stored in a glass carboy.

#### Experiment B-33

This experiment involved additional stability tests on phenyl boronic acid. Heating of a sample of the acid for 4 hours in an inert atmosphere ( $N_2$ ) at 200°C yielded only  $B_2O_3$ , indicating a non-oxidative thermal decomposition.

#### Experiment B-34

This was an attempt to form linear condensation products by reacting phenyl boronic acid with ethylene diamine, and with propylene glycol. The products formed, if any, were completely water soluble.

#### Experiment B-35

This was an attempt to polymerize phenyl boronic acid at low temperature in an anhydrous medium (dry ether at the boiling point). A very pure form of phenyl boronic acid was obtained, but no polymer.

#### Experiment B-36

This was the first experiment involving  $\text{BF}_3$  complexes. A tacky solid complex was formed from  $\text{BF}_3$  and ethanolamine. Various methods were used in attempting to bring about polymer formation, but only water soluble products were obtained.

#### Experiments B-37, B-38

Several experiments were carried out involving boric acid, rather than the phenyl derivative. In these two experiments, the condensation of boric acid with ethanolamine and with ethylene diamine was attempted. The products were in the form of viscous liquids, apparently having a low degree of polymerization, but all were water soluble.

#### Experiment B-39

This experiment was another attempt to bring about a polymerization of phenyl boronic acid, this time by bubbling  $\text{BCl}_3$  into a solution of phenyl boronic acid in anhydrous benzene, in the hope of splitting out  $\text{HCl}$ . The product obtained was not recovered phenyl boronic acid, but it was definitely non-polymeric.

#### Experiment B-40

This experiment was similar to Experiment B-39, but substituted tri-n-butyl borate for the benzene solution of phenyl boronic acid. No evidence of any reaction was observed, and 95% of the original ester was recovered.

#### Experiment B-41

This experiment was also similar to Experiment B-39, but used boric acid suspended in anhydrous benzene, instead of the benzene solution of phenyl boronic acid. No evidence of any reaction was observed.

#### Experiment B-42

This was an additional experiment on  $\text{BF}_3$  complexes, this one involving aniline. An off-white, amorphous product was formed, which, upon heating, gave off white fumes, and charred, but produced no polymeric material.

#### Experiment B-43

This experiment was the first attempt to prepare (4) dihydroxyfluoboric acid, based on the work of Bowlus and Niewland and involved this reaction:



The  $\text{BF}_3$  is then used again:



As the experiment was carried out, the product from the first reaction was not found in the proper receiver, but the

second reaction appeared to go as expected. A yield of 25 cc of a light yellow liquid was obtained after distillation of the crude product.

#### Experiment B-44

This was a second experiment on the preparation of  $H_3BO_2F_2$ , using  $BF_3$  directly from a cylinder. A yield of 32 cc of a light yellow liquid was obtained upon distillation of the crude.

#### Experiment B-45

This was the first experiment on complexes of  $H_3BO_2F_2$ . It was found that the addition of ether to  $H_3BO_2F_2$  forms  $H_3BO_3$  and the  $BF_3$ -ether complex.

#### Experiment B-46

This was a second experiment in preparing the n-butyl boronic acid by the ester method, in an effort to obtain a more satisfactory product than Experiment B-31 yielded. A fair sized first crop of crystals was obtained, with a melting range of 83-93°C. The evidence indicates that it still contained traces of n-butanol.

#### Experiment B-47

This was an experiment to determine the stability of n-butyl boronic acid. It was found that cold water hydrolyzed the acid readily. Additional results found are as follows:

- (1) When exposed to normal laboratory conditions for 23 days, the crystals were still largely in the form of butyl boronic acid. In 30 days, however, the crystals had largely changed to boric acid.
- (2) When held in an oven at 350°C, the butyl boronic acid decomposed completely in 20 hours or less (probably much less).
- (3) When held in a desiccator after 30 days storage, the crystals were about half decomposed.

#### Experiment B-48

This experiment concerned the production of material by heating the complex of ethylene diamine and dihydroxy-fluoboric acid. The product was in the form of a hard yellow solid, which when melted gave water soluble fibers. The solid did not burn when placed in a flame, but melted instead.

A further examination of the solid, including heating with additional  $H_3BO_2F_2$ , seemed to indicate that it was only impure  $B_2O_3$ .

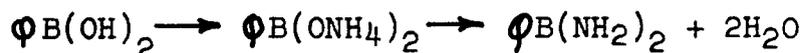
#### Experiment B-49

This was another experiment involving a complex of  $H_3BO_2F_2$ , this time with urea. The final product was a thick

white paste which was soluble in water, insoluble in ether. About 50 cc of ether was added to the batch, it was stirred thoroughly and filtered. The white amorphous product was then dried in a desiccator. Heating of a sample of the material produced fuming and then melting, but the material had no polymeric properties. Continued heating eventually produced glassy  $B_2O_3$ .

#### Experiment B-50

This experiment concerned attempts to produce  $\phi B(NH_2)_2$  through the sequence:



The procedure used was to dissolve the acid in anhydrous ether, bubble dry ammonia gas through it, and evaporate the solvent at room temperature. A white solid was obtained which upon heating sublimed, and then melted at 218-220°C. A mixed melting point with phenyl boronic acid was made, which indicated that the recovered material was the unreacted acid.

The experiment was repeated with several modifications, but again only unreacted acid was obtained.

#### Experiment B-51

This experiment covered the preparation of methyl boronic acid, from the methyl Grignard and tri-n-butyl borate. The Grignard was made using methyl chloride from a cylinder, with an absorption train as follows: dry trap, 3-necked agitated flask as the reactor, condenser, ether traps (2) for absorbing excess  $CH_3Cl$ . The reaction was difficult to initiate, and once started went rather slowly.

The reaction batch was worked up in the usual sequence of acid hydrolysis, ether extraction, separation, evaporation, steam distillation, crystallization, and filtration. A small yield of white, plate like crystals was obtained. The crystals were hygroscopic, and were originally soluble in ether. After an hour's exposure to laboratory air at 25°C, all the material appeared to have changed to boric acid.

#### Experiment B-52

This experiment repeated the procedure of Experiment B-51, in attempting to produce methyl boronic acid from the methyl Grignard and tri-n-butyl borate. The results were, similar, in that a small amount of low melting, ether-soluble material was isolated which rapidly absorbed moisture from the air, and changed to boric acid.

#### Experiment B-53

This experiment involved the preparation of n-hexyl boronic acid, through the usual Grignard-ester method.

After the Grignard addition was complete, the batch was allowed to warm up to room temperature, with agitation. The usual sequence of acid hydrolysis, ether extraction, neutralization, and vacuum steam distillation was followed. Upon final acidification, a considerable quantity of white crystals formed, which were filtered off, washed, and dried. The crystals were found to be ether soluble, and melted at 80-85°C. Recrystallization from ether gave material which melted at 86-88°C, vs literature data of 88-90°C for n-hexyl boronic acid. The yield of the hexyl boronic acid was 10%.

#### Experiment B-54

This experiment covered work on a sample of  $\text{BF}_3$  urea complex obtained from the General Chemical Division. Upon heating, the material first melted to a colorless liquid, which bubbled slowly, and then suddenly solidified to a pasty white mass. Further heating produced no further changes. Attempts to pull threads from the white residue were unsuccessful. Properties of the residue indicated that it was mainly  $\text{B}_2\text{O}_3$ .

#### Experiment B-55

This experiment covered the reaction of boric acid with glycerol. The mixture was heated in an oil bath, with evolution of 25 cc water. After cooling, the viscous mass set to a glass. Long, transparent glass-like fibers could be pulled from the molten material. The fibers slowly adsorbed moisture from the air, and became milky-white and wax-like, but were still quite strong. By dissolving a quantity in ethanol and allowing the solution to evaporate on a watch glass in a desiccator under nitrogen, a clear glassy film was obtained, which on exposure to air turned cloudy.

Samples of the melt, and of the fibers and films, were all water soluble.

A further sample of the melt was boiled in an evaporating dish, and then allowed to cool in a desiccator. The liquid set to a colorless smooth glass, which was chipped out, and found to melt at 55-65°C. Long threads could be pulled from the melt, but these also were easily soluble in warm water.

A small quantity of the melt was put in a three-necked flask, and heated for 3 hours under nitrogen. No apparent change occurred. Fibers could still be pulled, but all were water soluble.

#### Experiment B-56

This experiment was similar to Experiment B-55, but used octylene glycol in place of glycerol, and utilized a more efficient apparatus for removal of the water formed during the reaction. This equipment is discussed in Report AF 33(038) 23299-8.

The product was a mobile liquid, not a melt. A small

quantity was boiled in a beaker, but no change was noted.

#### Experiment B-57

This experiment was similar to the preceding two, but substituted polyethylene glycol, mol wt 200. The product was a semi-solid when cold, which could be drawn into fibers. They were not as strong as those produced from glycerol, and were soluble in cold water. A small amount of the material was heated in an evaporating dish to boiling, and then allowed to cool in a desiccator. No apparent change occurred.

#### Experiment B-58

This experiment was similar to the last three, except for using polyethylene glycol, mol wt 300, and the use of a nitrogen atmosphere during the condensation. The product was a water soluble, viscous mass, from which no fibers could be pulled.

#### Experiment B-59

This experiment duplicated Experiment B-56, except for using polyethylene glycol, mol wt 400. The product was a water soluble, viscous mass, from which no threads could be pulled.

#### Experiment B-60

This experiment concerned an attempt to prepare styryl boronic acid. The Grignard was made in an estimated 50% yield from  $\beta$ -bromostyrene, and was then reacted with tri-n-butyl borate, yielding two immiscible orange colored liquids. A procedure of acid hydrolysis, ether extraction, evaporation and cooling (no vacuum steam distillation) was then carried out, yielding a yellow solid, which was separated by filtration. The solid had an odor similar to  $\beta$ -bromostyrene, and this odor was not removed by crystallization from ethanol-water. The solid melted over the range 135-150°C, and appeared to give positive tests for boron and organo material. Based on the reaction for styryl boric acid, it was produced in 40% yield.

After several days drying in the desiccator it was again tested, and found to be entirely organic. Despite the fact that originally it gave a test for boron, no positive test could now be obtained.

#### Experiment B-61

This experiment concerned the preparation of additional amount of  $H_3BO_2F_2$ . During the distillation step, because of the slow rate of distillation in our unit, at atmospheric pressure, an attempt was made to vacuum distill the  $H_3BO_2F_2$ . Whatever the direct cause, a large amount of either  $H_3BO_3$  or  $B_2O_3$  formed on the walls of the receiver, during the distillation, resulting in a somewhat lower yield.

#### Experiment B-62

This experiment involved the reaction between  $H_3BO_2F_2$  and triethylene glycol. The ratio of reactants used was such as to make possible complexes of  $H_3BO_2F_2$  at both ether oxygens and both hydroxyl oxygens. The product was a viscous liquid, which was filtered and stored under nitrogen. No fibers could be pulled from it, so it was mixed with an additional amount of tri-ethylene glycol. The batch was then heated in an oil bath, and began to reflux at  $160^\circ C$ . The mixture darkened and finally became black. The product upon cooling was a semi-solid black paste, from which no fibers could be pulled. It was only partly water soluble. Because of the evident decomposition, the material was discarded.

#### Experiment B-63

This experiment involved the reaction between  $H_3BO_2F_2$  and p-phenylene diamine. The product was in the form of a water-soluble, light brown, amorphous powder, which melted at  $195-200^\circ C$ . It appeared non-polymeric so it was mixed with an additional amount of p-phenylene diamine, sufficient to bring the molar ratio of acid/amine to one. The mixture was heated for 2 hours in an oil bath, under vacuum. Some water distilled over, and after cooling, the product was a solid, from which fibers could be pulled upon heating slightly. The fibers were brittle and completely soluble in cold water.

#### Experiment B-64

The preparation of the light brown complex of p-phenylene diamine and  $H_3BO_2F_2$ , Experiment B-63, was repeated. Without mixing with additional diamine, the powder was heated in an oil bath, under vacuum. The heating was continued for 2 hours, during which time a small amount of water distilled over. Upon cooling, the product was in the form of a black solid, which was brittle, easily crushed, partially water soluble, and from which no fibers could be pulled.

#### Experiment B-65

This involved heating the complex of p-phenylene diamine and  $H_3BO_2F_2$ , with additional diamine in the following molar ratios:

	complex/amine
A	1:2
B	1:3
C	1:4

Heating of mixture A under vacuum resulted first in the slow distillation of an ammonia-smelling liquid at  $80-85^\circ C$ , then in a slowly increasing viscosity of the mass. Upon cooling, a solid black product resulted, partially water soluble. Some decomposition obviously occurred during the heating.

Complex B was heated only until evolution of the strongly ammonia smelling liquid (probably water) ceased. Short fibers could be pulled from the product, but all were water soluble.

Heating of C produced a porous, dark solid similar to that obtained from A.

#### Experiment B-66

This experiment concerned the reaction between phthalic anhydride, boric acid, and glycerol. Some preliminary experiments were run to see if heating boric acid with phthalic anhydride produced any sign of reaction, or evidence of the formation of a mixed anhydride, or of phthalic acid. No evidence of any such reaction was found.

A reaction was then attempted between the three components listed above, in amounts as follows:

$H_3BO_3$	.166 gm moles	0.5 gm equiv (10.3 gm)
$C_3H_5(OH)_3$	.166 gm moles	0.5 gm equiv (15.4 gm)
$C_6H_4(C_2O_3)$	.125 gm moles	0.25 gm equiv (18.5 gm)

The mixture was heated for  $2\frac{1}{2}$  hours on a hot plate, then allowed to cool. Long threads could be pulled, which were quite strong, but completely soluble in cold water.

#### Experiment B-67

Variations of Experiment B-66 were carried out, as follows:

	A	B	C	D
$H_3BO_3$	0.45 equiv	0.55 equiv	0.65 equiv	0.75 equiv
$C_3H_5(OH)_3$	1 equiv	1 equiv	1 equiv	1 equiv
$C_6H_4(C_2O_3)$	0.5 equiv	0.4 equiv	0.3 equiv	0.2 equiv

Heating was done by placing a beaker containing the batch on a hot plate, and was continued until all solid material had gone into solution. Inasmuch as the total of the acid constituents above is in all cases 0.95 equivalents, to each batch 0.05 equivalents of benzoic acid was added at this point to complete the reaction. The batches were then allowed to cool to room temperature. All products were viscous liquids; A was clear, however, while all the others were white. Liquid A had the highest viscosity, D the least.

Batch A was heated with additional phthalic anhydride, yielding a melt of much higher viscosity. Fibers could be drawn from the material, but all were completely water soluble. The material set as a glass at room temperature.

Experiment B-67A

This experiment was the first involving the attempted polymerization of the n-hexyl boronic acid prepared in Experiment B-53. A solution of n-hexyl boronic acid in anhydrous ether was refluxed for 24 hours. The ether was then distilled off at 22°C, 100 mm, leaving a residue of unchanged hexyl boronic acid.

Experiment B-68

At Lieutenant Luck's suggestion, because of the possibility of a complex forming between ether and the hexyl boronic acid (his suggestion actually concerned phenyl boronic acid) the above experiment was repeated, using dry benzene instead of ether. The results were the same, with unchanged hexyl boronic acid being recovered.

Experiment B-69

This experiment concerned stability tests on n-hexyl boronic acid. These were run at several temperatures below the melting point (86-88°C), as follows:

<u>Temp</u>	<u>Time</u>	<u>Results</u>
42°C	1 hr	Stable
62°C	1 hr	Partially decomposed
85°C	1 hr	Totally decomposed

The stability in water was also checked. It was found that the material is only very slightly soluble in either cold or hot water, and when placed in boiling water the bulk of the material remained on the surface and was apparently stable for a short period, even though molten. Any instability was apparently due more to the high temperature than to the presence of water.

Solubility data were also determined, as follows:

<u>Solvent</u>	<u>Remarks</u>
Water (cold)	Very slightly soluble
Water (hot)	Slightly soluble
Ether (cold)	Soluble
Benzene (cold)	Slightly soluble
Benzene (hot)	Soluble
CCl <sub>4</sub> (cold)	Very slightly soluble
CCl <sub>4</sub> (hot)	Slightly soluble
Methanol (cold)	Soluble
Methanol (hot)	Soluble

Stability was also checked after storage. After one month the material was still undecomposed in both the desiccator and after exposure to laboratory conditions.

#### Experiment B-70

This experiment concerned the reaction of p-phenylene diamine and boric acid. The above materials, in a 2/1 molar ratio, were heated in a small distilling flask under vacuum, with the  $H_3BO_3$  subliming badly, at times. About 4 cc of  $H_2O$  was collected in the receiver. No fibers could be pulled<sup>2</sup> from the product, and it was completely water soluble.

#### Experiment B-71

This experiment was similar to Experiment B-70, but phenyl boronic acid was used in place of boric acid. The temperature was also increased in an attempt to increase the extent of reaction. The product was a solid at room temperature, from which no fibers could be pulled. It was partially soluble in cold water, and completely soluble in hot.

#### Experiment B-72

This experiment was similar to Experiment B-71, but substituted lower melting m-phenylene diamine for the para derivative. Experimental conditions were otherwise the same. The product was a solid at room temperature, from which fibers could be pulled, but all were readily soluble in cold water.

#### Experiment B-73

This was an attempt to condense phenyl boronic acid by using more strongly dehydrating conditions. The equipment used consisted of a distilling flask equipped with a Dean and Stark "azeotroper" tube and condenser. A solution of phenyl boronic acid in anhydrous benzene was refluxed until the distillate collecting in the tube was clear, then 1 cc of  $POCl_3$  was added. A total of about 0.4 cc of water separated out in the tube. After cooling overnight, the product consisted of a brown solution containing a small amount of solid. The solid was separated by filtration and proved to be  $B_2O_3$ . The solution was evaporated under vacuum, yielding a brown solid melting over the range 195-215°C. It appeared to be impure phenyl boronic acid.

#### Experiment B-74

This experiment was similar to Experiment B-73, but n-hexyl boronic acid was used in place of phenyl boronic acid, and higher boiling ethyl benzene in place of benzene. The reflux (136°C) was maintained for 4 hours, resulting in the separation of 3 cc of  $H_2O$ . The solution was filtered, then evaporated under air. The product was a yellow, paste-like solid, which was found to be completely water soluble.

### Experiment B-75

This experiment was similar to Experiment B-70, covering the reaction of boric acid and p-phenylene diamine, but a solvent and an "azeotroper" tube were used, in place of heating under vacuum. Only 1 cc of H<sub>2</sub>O collected in the Dean and Stark tube in the 5 hour period. Much of the solid reaction material did not dissolve. At the end of the 5 hours this was filtered off, and examined. It appeared similar to the material charged in, and was water soluble. The filtrate was evaporated under vacuum, yielding another water soluble non-polymeric material.

### Experiment B-76

This experiment was carried out according to directions furnished by Professor M.A. Rollier of the Institute of General and Analytical Chemistry, Polytechnic School, Milan, Italy. The product isolated from the reaction of phenyl Grignard and BCl<sub>3</sub>, followed by hydrolysis, ether extraction, evaporation, and distillation, gave cuts as follows:

#### Fraction 1

	<u>Temp and Press</u>	<u>Description</u>
Rollier	40-80°C/20-25 mm	Colorless liquid
Observed	35-50°C/0.7 mm	Colorless viscous liquid

#### Fraction 2

Rollier	80-105°C/15 mm	Yellow liquid
Observed	50-67°C/0.7 mm	Yellow liquid

#### Fraction 3

Rollier	130-175°C/15 mm	Yellow-pink vapor, yellow-brown gelatinous liquid
Observed	None	None

Fraction 1 was found to be soluble in cold and hot water, insoluble in cold or hot benzene, ethyl acetate, CCl<sub>4</sub>, and dichloroethylene. This fraction did not give a test for boron, and showed no significant amount of organic material. However, the material did not appear to be water, and gave white precipitates with both acetone and methanol.

Fraction 2 was found to be insoluble in cold water, slightly soluble in hot, and soluble in methanol, benzene, ethyl acetate, and ethylenedichloride. This fraction did not give a test for boron, but was definitely organic.

A considerable amount of still residue was left, which

was extracted with ether, filtered, and the ether evaporated. The resulting solid (A) was dark brown and non-homogeneous. It was found to be insoluble in cold water, slightly soluble in hot water, and in hot or cold phenylene diamine, 6N NaOH, benzene,  $\text{CCl}_4$ , and dichloroethylene, and partially soluble in acetone, ethyl acetate, and methanol. The material gave a strong positive test for boron.

The brown solid (A), when heated, did not melt completely below  $300^\circ\text{C}$ , but at about  $150^\circ\text{C}$  partially sublimed colorless needles. Vacuum sublimation in a special apparatus involving a dry ice-acetone condenser, oil bath, and dry ice trap was tried, and gave an incomplete separation of a yellow-white sublimation product, leaving a brown residue (B).

Sublimation of the residue (B) was continued at atmospheric pressure. A small amount of both white and yellow crystals formed on the condenser surface.

Attempts were made to separate solid (A) into its components by fractional crystallization, but no satisfactory solvent could be found.

A chromatographic separation of solid (A) was then attempted, using ethyl acetate as the solvent and activated alumina as the absorbent. The preliminary extraction of A with ethyl acetate gave a fluorescent solution, which showed a positive test for boron. A brown residue was left which did not give a positive boron test. The fluorescent solution was run slowly through a  $1/2$ " x 18" chromatographic column. Evaporation of the solvent from the solution which passed through the column yielded a brown oil as the residue. This oil did not show a positive boron test.

Elution of the column with ethyl acetate-methanol, followed by evaporation of the solvent, gave a white crystalline product contaminated with small amounts of the dark brown oil. The white crystals gave a positive boron test.

The chromatographic separation was repeated, using anhydrous  $\text{Na}_2\text{SO}_4$  in place of activated alumina as the adsorbent. Similar results were obtained, with the product being a small amount of white crystals contaminated with brown oil.

The two small yields of impure white crystals were combined, and after testing various solvents were finally purified by washing in  $\text{CCl}_4$ , recrystallizing in ethyl acetate, and washing again in  $\text{CCl}_4$ . From melting point and solubility data it was concluded that the crystals were impure phenyl boronic acid.

### Experiment B-77

This experiment was undertaken to determine properties of maleic anhydride-glycerol resins, with boric acid substituted for some of the maleic anhydride.

#### Experimental conditions

	A	B	C	D
Maleic anhydride	0.8 equiv	0.6 equiv	0.4 equiv	0.2 equiv
Boric acid	0.1	0.3	0.5	0.7
Glycerol	1.0	1.0	1.0	1.0

Each batch was heated until all reactants were in solution (1-2 hours). In each case 0.1 equiv of benzoic acid was then added, and the heating continued for a total of 4 hours. In all cases the solutions became viscous and turned yellow. Long, strong fibers could be pulled from each sample of resin, but all were readily soluble in hot water, although less soluble in cold water than the glycerol-phthalic anhydride products of Experiment B-66.

The polymers were found to be readily soluble in acetone and methanol, insoluble in ether. Attempts to form crystals by precipitation from acetone and methanol, through the addition of ether, yielded oils which solidified to glasses.

### Experiment B-78

This experiment was similar to Experiment B-77, but fumaric acid was substituted for maleic anhydride. The addition of benzoic acid was also eliminated.

#### Experimental conditions

	A	B	C	D
Fumaric acid	0.7 equiv	0.7 equiv	0.7 equiv	0.7 equiv
Boric acid	0.1	0.2	0.3	0.4
Glycerol	1.0	1.0	1.0	1.0

Each batch was heated for four hours on a hot plate. In none of the cases did the solid go entirely into solution, but considerable water was evolved from each beaker. The products were very viscous and quite rubbery. Samples of rubbery material from A and B were either insoluble, or very slowly soluble, in cold water, and difficultly soluble in hot water.

### Experiment B-79

Because of the properties displayed by the products of Experiment B-78, this experiment was undertaken in an effort to increase the extent of reaction.

#### Experimental conditions

Fumaric acid	1.4 equiv (81.2 gm)
Boric acid	0.2 equiv (4.2 gm)
Glycerol	2 equiv (61.4 gm)

Heating was done in a Claisen flask, under vacuum, with an oil bath and a receiver. The heating was continued for 5 hours, with 23 ml or 1.2 equivalents of water being collected. The product was still sparingly soluble in cold water, but when dissolved in water the solution left a greasy film difficult to remove.

#### Experiment B-80

As a standard of comparison, it was decided to prepare glycerol-phthalates, maleates, and fumarates, without the substitution of boric acid.

#### Experimental conditions

A. Phthalic anhydride	1.0 equiv
Glycerol	1.0 equiv
B. Maleic anhydride	1.0 equiv
Glycerol	1.0 equiv
C. Fumaric acid	1.0 equiv
Glycerol	1.0 equiv

After heating each batch in a beaker on a hot plate for 6 hours, followed by cooling, A formed a clear yellow glass, B and C formed white solids, C being somewhat rubbery. All were slowly soluble in hot water, insoluble in cold.

#### Experiment B-81

This experiment was an attempt to achieve a greater extent of reaction than that indicated by the products of either Experiments B-79 or B-80.

#### Experimental conditions

Fumaric acid	1.0 equiv (58 gm)
Boric acid	1.0 equiv (20.6 gm)
Glycerol	2.0 equiv (61.4 gm)
Ethyl benzene (dry)	200 cc

The condensation flask was set up with a Dean and Stark water separating tube or "azeotroper". At the end of 3 hours, 28 cc of H<sub>2</sub>O had collected, as compared to a theoretical amount of 36 cc. At the end of this 3 hour period, no additional water was separating, so 250 cc of anhydrous methanol was added, and the mixture refluxed for 8 hours. Upon cooling, the light orange mixture separated into two layers, an upper one of methanol, and lower one of ethyl benzene. A small amount of undissolved solid was also present.

The upper methanol layer was decanted into a Claisen flask, and the solvent removed by use of vacuum. The deep orange residue foamed violently toward the end of the distillation, and solidified upon cooling. It had to be chipped out, and was in the form of a clear, strong resin, only slightly soluble in cold water. It gave good tests for both boron and organic material.

#### Experiment B-82

This was similar to Experiment B-81, except that phthalic anhydride was used in place of fumaric, and benzene in place of ethyl benzene.

#### Experimental conditions

Phthalic anhydride	1.0 equiv (74 gm)
Boric acid	1.0 equiv (20.6 gm)
Glycerol	2.0 equiv (61.4 gm)
Time	93 hours

The unit used was a three-necked flask, equipped with stirrer, condenser, and Dean and Stark tube. After 93 hours, only 18 cc of H<sub>2</sub>O (36 cc theory) had separated. The mixture was cooled and the benzene decanted off. The residue was putty-like, and very unlike the other polymers. 200 cc of anhydrous methanol was added, and the batch refluxed until the solid went into solution. The solution was then evaporated on a hot plate, yielding a yellow brown, soft, sticky, low-melting resin, completely soluble in cold water.

#### Experiment B-83

This experiment repeated the conditions of Experiment B-82, but ethyl benzene replaced the benzene, and a fractionating column, plus condenser and receiver were used in place of the condenser and azeotroper.

#### Experimental conditions

Phthalic anhydride	1.0 equiv (74 gm)
Boric acid	1.0 equiv (20.6 gm)
Glycerol	2.0 equiv (61.4 gm)
Ethyl benzene	200 cc

The water and ethyl benzene in the receiver were separated at intervals, and the ethyl benzene dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and returned to the reactor. After 3 hours no further water was removed. The solution was refluxed for 42 hours and then allowed to cool. A gray-green, hard, brittle solid was obtained, which slowly picked up moisture from the air and developed an oily film. The material appeared to be insoluble in cold water, hot or cold ether, hot or cold CCl<sub>4</sub>, cold ethyl acetate and cold benzene. It was slowly soluble in hot water, hot ethyl acetate, and hot benzene, and dissolved readily in methanol and acetone.

#### Experiment B-84

A quantity of the resin from Experiment B-83 was melted and poured between two thin sections of plywood. The material was then held in a press at 2000 psi, 250°F, for 1/4 hour. The material did not reach a thermosetting stage, but after cooling bonded the sections of plywood firmly together.

The above procedure was repeated, using powdered resin at room temperature, 2000 psi, for 2 hours. No bonding was achieved.

The procedure was again repeated, at 2000 psi, 150°F, 2 hours. Good bonding was again secured, but no thermosetting took place.

All samples of the pressed resins, when exposed to moisture in the air, rapidly became sticky and lost their ability to bond the plywood firmly.

#### Experiment B-85

This experiment repeated the condensation of Experiment B-83, using the same procedure and apparatus, with reactants in the following amounts:

Glycerol	3 equivalents
Phthalic anhydride	2 equivalents
Boric acid	1 equivalent
p-xylene (solvent)	150 cc

After 14 hours, only 52% of theory of water had been separated; no additional water formed, so the material was refluxed for 5 hours and then allowed to cool. A light yellow resin formed, which was hard and smooth in a desiccator, but which picked up moisture slowly upon exposure to laboratory air, becoming quite sticky. Its melting range was 40-60°C, and its solubility characteristics were similar to those reported in Experiment B-84,

#### Experiment B-86

Because the water sensitivity of the resin from Experiment B-85 might have been due to the incompleteness of reaction, with the consequent presence of large numbers of hydroxyl groups, an attempt was made to complete the reaction by heating a portion of the resin with benzoic acid for 1 hour. However, the melting range was increased only slightly (to 45-65°C) and solubility characteristics were relatively unchanged.

A sample of this modified resin was held between two thin sheets of plywood at 2000 psi, 150°F, for 2 hours. After cooling it appeared to bond the plywood very well, but soon absorbed moisture from the air, turned milky white and sticky, and lost its good bonding properties.

A sample of the original resin of Experiment B-85 was also held at 2000 psi, 150°F, for 2 hours, and was found to have similar properties.

Experiment B-87

Experiment B-85 was repeated, changing the reactants to the following:

Glycerol	4 equivalents
Phthalic anhydride	3 equivalents
Boric acid	1 equivalent
p-xylene (solvent)	150 cc

After 10 hours, water ceased to come over, at which point only 56% of theory had collected. The material was then refluxed overnight and cooled. A yellow resin melting at 45-65°C was obtained. When held between two thin sheets of plywood at 2000 psi, 150°F, 2 hours, and cooled, it displayed good bonding but had the usual moisture sensitivity, and turned milky white.

Experiment B-88

This experiment concerned the preparation of ethoxyboron dichloride.

Experimental conditions

$(C_2H_5)_2O$	189.7 gm
$BCl_3$	60 gm
Temperature	In ice bath

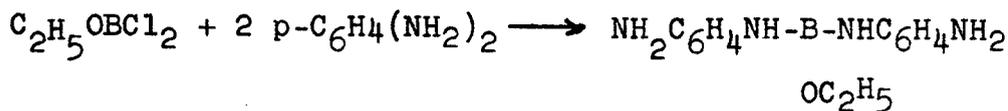
The gaseous  $BCl_3$  was bubbled into the ether, held in an ice bath, over a period of two hours. The product was then distilled, yielding the following fractions:

30-65°C	117 gm, mainly unreacted ether
65-100°C	47 gm, mainly ethoxyboron dichloride

The second fraction was redistilled, and the cut from 75-90°C, most of which boiled at 82-83°C (vs 78°C from Rollier), was retained. The yield was approximately 34%. The ethoxyboron dichloride fumed in air and reacted violently with water.

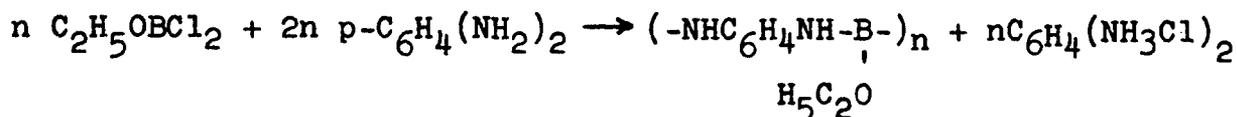
Experiment B-89

This experiment concerned an attempt to react ethoxyboron dichloride with p-phenylene diamine:



(as the hydrochloride?)

or



#### Experimental conditions

$\text{C}_2\text{H}_5\text{OBCl}_2$	0.043 gm moles (5.4 gm)
$\text{p-C}_6\text{H}_4(\text{NH}_2)_2$	0.086 gm moles (9.3 gm)

The diamine was added continuously to the cold dichloride. No evidence of reaction was observed. The mixture was then slowly heated up to reflux (150°C), but no visible reaction occurred. After 3 hours heating, the mixture was allowed to cool. The resulting tan solid was dissolved in hot methanol, which, upon cooling, gave brown crystals. The crystals gave only a faint test for boron.

#### Experiment B-90

Experiment B-76 was repeated, again using the directions furnished by Rollier. The final reaction product was a yellow semi-solid, with green spots. After heating for 3 hours it changed to a steel-gray solid.

The solid was ground up and added to cold water, giving a vigorous reaction. The product was in the form of a dark oil, greasy to the touch. It was extracted with ether, the ether evaporated off, and the solution vacuum distilled. Fractions 1 and 2, a colorless and a yellow liquid, respectively, were again obtained. In addition, a white gelatinous material formed between the two cuts. It was present in much larger amounts than described by Rollier, and was water insoluble. However, it gave no test for boron.

#### Experiment B-91

This experiment involved reacting ethoxyboron dichloride and ethylene diamine. A violent reaction occurred, with evolution of heat and white fumes. After a 10 hour reflux, the batch was cooled, and the pasty material filtered off and dried. The resulting solid gave tests for boron and organic material but was very soluble in cold water.

#### Experiment B-92

Ethoxyboron dichloride and p-phenylene diamine, in an equimolar ration, were reacted in benzene solution. The final products, isolated after an acetone extraction, appeared to be boric acid and recovered p-phenylene diamine.

#### Experiment B-93

Experiment B-92 was repeated, using a 2/1 molar ratio of ethoxyboron dichloride to p-phenylene diamine, with results similar to those of Experiment B-92.