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WADC TECHNICAL REPORT 55-26

PART IV

ASTIA DOCUMENT No. AD 110403

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RESEARCH ON BORON POLYMERS

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RUTGERS UNIVERSITY

SEPTEMBER 1956

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SEPTEMBER 1956

MATERIALS LABORATORY

CONTRACT No. AF 33(616)-2057

PROJECT No. 7340

WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

FOREWORD

This report was prepared at the School of Chemistry, Rutgers University, New Brunswick, New Jersey under USAF Contract No. AF 33(616)-2057. This contract was initiated under Project No. 7340, "Rubber, Plastic and Composite Materials", Task No. 73404, "Synthesis and Evaluation of New Polymers", and was administered by the Organic Materials Branch, Materials Laboratory, Directorate of Research, Wright Air Development Center, with Lt. Douglas A Rausch acting as project engineer.

This report covers the period of work from December 1955 through June 1956 and is the final part of this work.

The personnel assigned to this project were, Dr. William L. Ruigh, Principal Investigator; Dr. A. D. Olin as full time research assistant from 1 January 1956 to June 1956; Mr. N. G. Steinberg as part time assistant until 6 June 1956 and full time thereafter and Dr. P. A. van der Meulen as staff consultant. A secretary part time was assigned.

ABSTRACT

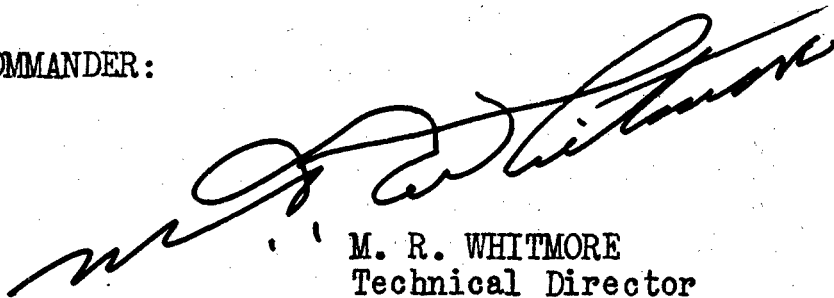
Tri-B- β -chloroborazole has been prepared from β -chlorovinylboron dichloride and ammonia. It is unstable and in the presence of polar solvents forms either cyclic or long chain polymers.

Large samples of 100 grams or more of Tri-B-b-butylborazole, Hexabutylborazole, and Tri-N-Methyl-tri-B-n-butylborazole were prepared for evaluation.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



M. R. WHITMORE
Technical Director
Materials Laboratory
Directorate of Research

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I. INTRODUCTION

This report covers a project on "Research on Boron Polymers" for the period from December 1955 through June 1956. This work is a part of an Air Force continuous study program, the broad objective of which is to prepare and investigate new hydrolytically stable polymeric materials possessing exceptional fuel and oil resistance, high thermal stability and other properties of critical importance for specialized Air Force Applications. Another purpose of this work, which has developed particularly in the past year, is the preparation of certain materials for evaluation as hydraulic fluids and lubricants.

Since the inception of this work at Rutgers in June 1953, fourteen progress reports have been issued and are now out of print (A-1 to A-9 and B-1 to B-5 inclusive). This material has or is being incorporated in WADC Technical Report 55-26 Part I, II, III, and IV, (1)(2)(3). WADC Technical Report 55-26, Part I consists of a literature survey in the field of boron polymers together with pertinent references in the general field of inorganic and semi-inorganic polymers(1). The second part of this report (WADC Technical Report 55-26, Part II) describes the experimental work on the project carried out over the eighteen month period, 1 June 1953 to 30 November 1954 (2). The third part of this report (WADC Technical Report 55-26, Part III) describes further experimental work during the period December 1954 to December 1955 (3). The third part of the report deals primarily with a new synthesis of alkyl and aryl boron substituted borazoles and an intensive study of the synthesis of the intermediate aryl and alkyl boron dichlorides. Attempts to form the "scorpion" boronic acids via the Marxer reaction are also reported.

The present report deals primarily with the synthesis of the alkyl and aryl boron dichlorides used as intermediates for the synthesis of boron substituted borazoles and the synthesis of a 100 gram sample of tri-B-n-butylborazole for evaluation. Also included is a study of the analysis of organo-boron compounds with particular emphasis on the development of a method for the analysis for boron in borazoles.

Manuscript released by author 31 July 1956 for publication as a WADC Technical Report.

At the end of the report period ~~syntheses~~ were being carried out on the preparation of tri-N-methyl-tri-B- β -butylborazole and this will be reported in the experimental section.

Considerable effort was also spent in the preparation of B- β -chlorovinylborazole which, as might be expected, appears to polymerize to either long chain or cyclic higher polymers. B- β -chlorovinylborazole itself is somewhat unstable for practical use but the results point the way to the possible eventual solution of the problem of the preparation of boron polymers stable at high temperatures.

II. LITERATURE SURVEY AND DISCUSSION OF EXPERIMENTAL RESULTS

As reported earlier (3) tri-B-phenyl borazole was found to be a solid, m.p. 184° C. Also in our disproportionation of tributylborine with boron trichloride over an aluminum chloride catalyst (2) the yield of the low temperature reaction was 10% or less. At the Minneapolis Meeting of the American Chemical Society, we learned that higher yields might be obtained using a high pressure autoclave and omitting the aluminum chloride catalyst. Due to delays in obtaining reports on this work coupled with inadequate facilities for high pressure reactions with toxic and pyrophoric materials we suspended the work on the n-butylboron dichloride in spite of an 160 gram stockpile. Eventually we purchased 1 kilogram of n-butylboron dichloride from a custom supplier of organic intermediates .

Since the tri-B-phenylborazole was a solid, the intermediate for the tri-B-n-butylborine temporarily unavailable and because of the interest attached to the synthesis of a borazole with reduced resonance possibly leading to linear or cyclic high molecular weight polymers, we decided to synthesize the tri-B- β -chlorovinylborazole from β -chlorovinylboron dichloride and ammonia.

It might be expected that the π electrons of the vinyl double bonds might tend to fill out the six electron shell of the boron atoms and thus diminish the resonance induced by donation of electrons from the nitrogen atoms in borazole.

The intermediate required, β -chlorovinylboron dichloride and the corresponding acid were first described by Arnold in two patents assigned to Du Pont. Later Borisov prepared the compound from the reaction of a mercury salt, β -chlorovinylboronmercury chloride with boron trichloride (6). The dichloride was prepared by Arnold from the reaction of acetylene at atmospheric pressure with boron trichloride when passed over a charcoal supported mercurous chloride catalyst at 150-300° C.

In the Du Pont work the gases were metered into the inlet end of the catalyst tube and contact times carefully controlled. A ratio of boron trichloride to acetylene of 1.5

1 Chemicals Procurement Co., 550 Fifth Ave., New York, 36, NY.

to 1 was maintained with a catalyst contact time of 8-12 seconds. Without the engineering facilities available to Du Pont and also because our boron trichloride recirculating apparatus developed for phenylboron chloride seem to offer certain advantages over the metering method (particularly with regard to BCl_3) we rebuilt our recirculator with a new catalyst chamber. Instead of using a furnace as formerly described, we used a nichrome wire heating coil with a minimum of insulation. This was done to avoid the difficulties of controlling the strongly exothermic reaction in the earlier type of set up.

As described in the experimental portion, the initial run gave an excellent yield of product with little difficulty. The crude product appeared on distillation to be substantially free of bis-chlorovinylboron monochloride and tris-chlorovinylborine. This was rather expected since the excess boron trichloride recirculating in the system would tend to minimize the formation of these products.

The interesting observation was made that acetylene and boron trichloride formed a solid crystalline addition product. This product liquified and then vaporized in the presence of an excess of boron trichloride. Presumably the product is formed through the π electrons of acetylene filling the highly "acceptor" boron shell of electrons in BCl_3 (from 6 to 8 in the addition compound).

The β -chlorovinylboron dichloride was hydrolyzed to the free acid, m.p. 128-129°. This acid was also described in Arnold's second patent (5). We found the acid to be very unstable in alkalis or aqueous solutions of amines giving free acetylene, and splitting out hydrochloric acid. A re-reading of the abstract of the article by Borisov (6) revealed the mention of the fact that the boronic acid gave 100% yields of acetylene in the presence of 10% aqueous NaOH. Borisov, incidentally, prepared the intermediate from chlorovinyl mercury chloride with BCl_3 in kerosene as a solvent. The Arnold patent does not mention this instability to alkalis and in fact is somewhat misleading in this respect since the following statement is made "Aqueous solutions of chlorovinylboronic acid can be used to maintain a pH of about 4 against the addition of alkalis or ammonia".

The research on the synthesis of tri-B- β -chlorovinyl borazole occupied a major portion of the program from 1 January

until 1 March 1956. Considerable difficulty was encountered in attempting to isolate pure materials from the mixture resulting from the reaction of β -chlorovinylboron dichloride and ammonia in benzene. The bulk of the product was probably the borazole but this was accompanied by transformation products, with some of apparently considerably higher molecular weight.

The experimental problems encountered in the separation of these reaction products was very greatly complicated by the ease of decomposition of some of these fractions. Both insoluble products and hydrochloric acid were formed during standing or heating of these materials. This decomposition was very marked in the runs with benzene as the solvent.

With the thought that less decomposition and possibly less tendency towards higher polymerization of these materials could be attained by filling the acceptor shell of the boron atom with a suitable donor we replaced the inert solvent benzene with ethyl ether. The formation of a loose addition compound appeared likely. The addition of the β -vinylboron dichloride to ether resulted in a considerable evolution of heat. Tetrahydrofuran was not used since very satisfactory results were obtained with ethyl ether. As described in the experimental section, reaction with ammonia gave a good yield of crystalline product which appears to be tri-B- β -chloro-vinylborazole. Analyses of the compound are still pending due to the temporary unavailability of the microanalyst and we hope to have these results included in the experimental section.

The product from the reactions in ether showed much greater stability than the earlier materials obtained from benzene. The transformation or polymerization of the borazole into insoluble or partially soluble materials was dependent on the nature of the solvent. Strongly "polar" solvents such as dioxane, acetone and dimethylformamide tended to accelerate or induce these transformations.

Without further experimental work the nature of these polymers whether formed of cyclic or linear units or mixtures cannot be ascertained. The least soluble polymers were only partially soluble in dimethylformamide and the more soluble materials dissolved in acetone but appeared as glassy solids

when their solutions were evaporated.

Theoretically, one might speculate that the π electrons of the vinyl double bonds partially filled the acceptor orbitals of the boron atoms in the borazole. The resonance in the borazole ring would then be diminished and one might expect either higher molecular weight cyclic or linear polymers to form. Much further experimental exploratory work is necessary in this field before such speculations can be verified.

Because of the request for large samples of boron substituted borazoles for practical evaluation the major portion of the work from 1 March 1956 to 1 May 1956 was devoted to scaling up the preparation of phenylboron dichloride by the modified method of Pace (7). Due to accidental poisoning of the catalyst first with mercury and then in the next preparation with an influx of hydrogen sulfide from the adjoining student laboratories much time was lost. Finally, when these conditions were rectified the yields and conversion rates were only 10-20% of that expected, based on early work. The difficulties lie in one or more several broad areas: (1) Technical boron trichloride has a variable composition and may be responsible since all other materials were highly purified; (2) The early runs were made in a catalyst tube surrounded with an air space in which the registering thermocouple was placed. In the scaled-up apparatus, a direct wrapped furnace, was used and the comparative temperature measurement was in doubt; (3) For unknown reasons the 2% palladium catalyst on charcoal may not have duplicated our earlier catalysts.

In the final run on this preparation a special grade of boron trichloride was obtained from the Stauffer Chemical Company through the courtesy of Dr. Bashour and Mr. Heiss. This material contained only 0.003% sulfur as compared to up to 0.2% found in some of the earlier technical grades used by us. We unfortunately changed the brand of benzene (reagent A.C.S. standard) used in this run. This run was marked by a practically negligible yield of phenylboron dichloride but a relatively large amount of biphenyl which was not apparent in earlier runs. Further, marked carbonization occurred even beyond the heated section of the catalyst tube. After about six hours running time the 625 ml. catalyst bed became completely plugged and the run was discontinued. Further work

on this reaction is required in order to determine the cause of the variability in conversion time, yield and the nature of the products. The yields obtained on the larger scale apparatus were only 10-20% of that expected on the basis of earlier small scale runs.

Due to discrepancies in the analyses of B-triphenylborazole a review of the procedures was undertaken. Since boric acid is not a particularly good standard substance, we propose to use the diethanolamine ester of benzeneboronic acid (2)(8)(9)(10). This substance has the marked advantage of being a stable organoboron compound of uniform composition with no evidence of hydration or solvation. Two lots of the material were made up for standard samples by a new and simplified procedure.

After starting this work we noted that J. M. Thoburn with D. D. DeFord (11) at Northwestern University had obtained excellent results in the analysis of this ester by their electrolytic oxidation method.

The problems associated with the analyses of substituted borazoles have not been solved although progress has been made. Preliminary digestion of the borazole or a nitrogen containing organo-boron compound in sulfuric acid with 30% hydrogen peroxide leads almost invariably to low results. These low results are obtained in spite of subsequent digestion in alkaline peroxide solutions. The results are particularly low if the sulfuric acid mixture is heated just to the fuming point.

Preliminary decomposition of the sample of ester in 50% sulfuric acid without the addition of peroxide followed by an alkaline peroxide digestion seems to give fair results. Further work is necessary and peroxide fusions may be the eventual answer to this problem. In the titrations themselves, the electrometric methods of Rieman (12)(13) have been used. The method of Thoburn and De Ford (11) has not been tried due to lack of time before the expiration of this contract. We had hoped to develop or adapt distillation methods both for the nitrogen and the boron in our materials but time has been lacking. With the increased interest in boron compounds, we feel certain that adequate methods will soon be developed or published which will be adaptable to the analyses of borazoles.

The final phase of this project has been the preparation of large samples for evaluation. With the exception of some work on the tri- β -chlorovinylborazole, practically no chemical work has been done on the end products themselves, the boron substituted borazoles. In fact, except for the physical and analytical data reported earlier (3), we had not made any borazole in quantity after the initial early one and three gram runs until the first bulk preparation run in May 1956. This run gave 51.6 grams of material of which 50 grams was immediately delivered to the Materials Laboratory for evaluation. A yield of 71% (or 81% if the still residue is included) was obtained in our first trial large scale run from gaseous ammonia and n-butylboron dichloride in ether solution.

Details of the large scale runs on tri-B- β -butylborazole will be found in the experimental section.

As this report is being written we are extending the reaction to include the N-methyl and possibly the N-butyl (hexabutylborazole), analogues of the tri-B- β -butylborazole. Since the techniques will be very similar, details will be found in the experimental section.

In the limited time available we have not investigated the problem of preparing high polymers from alkyl and aryl boron dihalides and bifunctional amines. Intermediates with an amino group at one end and a donor group such as another amino group or a dialkyl amine at the other end would be of interest. An alcohol, ether or mercapto group could also act as the donor half. Heterocyclic amines would also be of interest. This approach was outlined in Part III of this report (p. 15 ref. 3) but our time has been taken up primarily in the study of the preparation of the boron dihalides for use in the borazole synthesis and in the production of bulk samples for evaluation by the WADC Materials Laboratory.

The work on the tri- β -chlorovinylborazole does indicate that the borazole ring may open to give high molecular weight linear or cyclic polymers when the open valence orbitals tend to become filled and the boron atoms approach the quadricovalent state. In the case of the tri- β -chlorovinylborazole the electrons come from the π electrons of the vinyl group whereas the approach outlined in Part III (3) deals with filling the boron orbitals with an external but "anchored" dative pair from an atom such as nitrogen or oxygen.

In conclusion, this exploratory and preparative project carried out over the contract period 1 June 1953 through 31 July 1956 has successfully attained the desired objectives and opened up a very large and interesting field of work for the further investigation of boron polymers and high temperature fluids in addition to a considerable amount of information on the synthesis of certain organo-boron compounds required as intermediates.

III. CONCLUSION

A general conclusion regarding the objectives obtained during the entire contract period has been stated in the preceeding paragraph.

During the period covered by this part of the report we have reached the following conclusions.

As expected, with an adequate supply of alkyl or aryl boron dihalide, the synthesis of borazoles in bulk may readily be accomplished by reaction with a suitable amine in either an inert solvent such as benzene or a donor solvent such as ether. The yields range from 70-95%.

The formation of linear or cyclic high polymers from the opening of the borazole ring might be accomplished by filling or partially filling the open orbitals of the boron atoms of the borazole.

The catalytic synthesis of phenylboron dichloride from benzene and boron trichloride by Pace's method (7) is not as yet reliable and further study is required both on the conditions of the reaction, the catalyst, and the purity of the materials employed.

The analysis of organo-boron compounds such as borazoles has not as yet been fully solved in our laboratory but reasonably accurate results have more recently been attained.

IV. PLANS AND RECOMMENDATIONS

With the expiration of the contract on 31 July 1956 and the annual leave accruing to personnel involved, the plans for the remainder of the contract period are to prepare as much as possible of the bulk samples of borazoles for evaluation by the Materials Laboratory.

V. EXPERIMENTAL

1. Apparatus for the Preparation of β -chlorovinylboron dichloride

The apparatus designed and built for the preparation of phenylboron dichloride (see Part III, p. 27, Figure II, catalytic apparatus) (3) and Figure I p. 13 of this report was rebuilt in a new location and modified for the synthesis of β -chlorovinylboron dichloride. The main difference was the substitution of a nichrome-asbestos-paper covered catalyst chamber of larger capacity than could be handled by the Lindberg furnace or any other readily available furnace. A catalyst chamber having about 400 ml. capacity was constructed of 40 mm. outside diameter pyrex tubing and terminated by a pair of 24-40 standard taper joints as shown in the diagram. Indentations were made to hold the glass Raschig rings. The total length of the furnace and joints was 65 cm. The heated section 35 mm. in length was wrapped with 22 feet of No. 24 B and S. nichrome wire with about one quarter inch separation between turns. Before winding the furnace, an enamel covered No. 24 B.S. gauge iron-constantan couple was placed next to the glass and the tube wrapped with a single layer of asbestos paper moistened with sodium silicate. After winding with the nichrome wire, an additional layer of asbestos paper with silicate was used as an outer cover. Less insulation than normally was used in order to allow for ready control of temperature particularly in view of the strongly exothermic nature of the reaction of acetylene with boron trichloride. Table I gives the characteristics of the catalyst furnace with various voltages as supplied by an 8 ampere variac. With these tests the furnace was judged satisfactory since the operating temperature was expected to be about 150° C.

TABLE I

Furnace Temperatures as a Function of Impressed Voltage

<u>Voltage</u>	<u>Temperature ° C.</u>
50	85
60	120
70	152
80	222

The furnace was then assembled with the apparatus as shown in the diagram and the whole set-up checked for leaks under a vacuum of 1 mm.

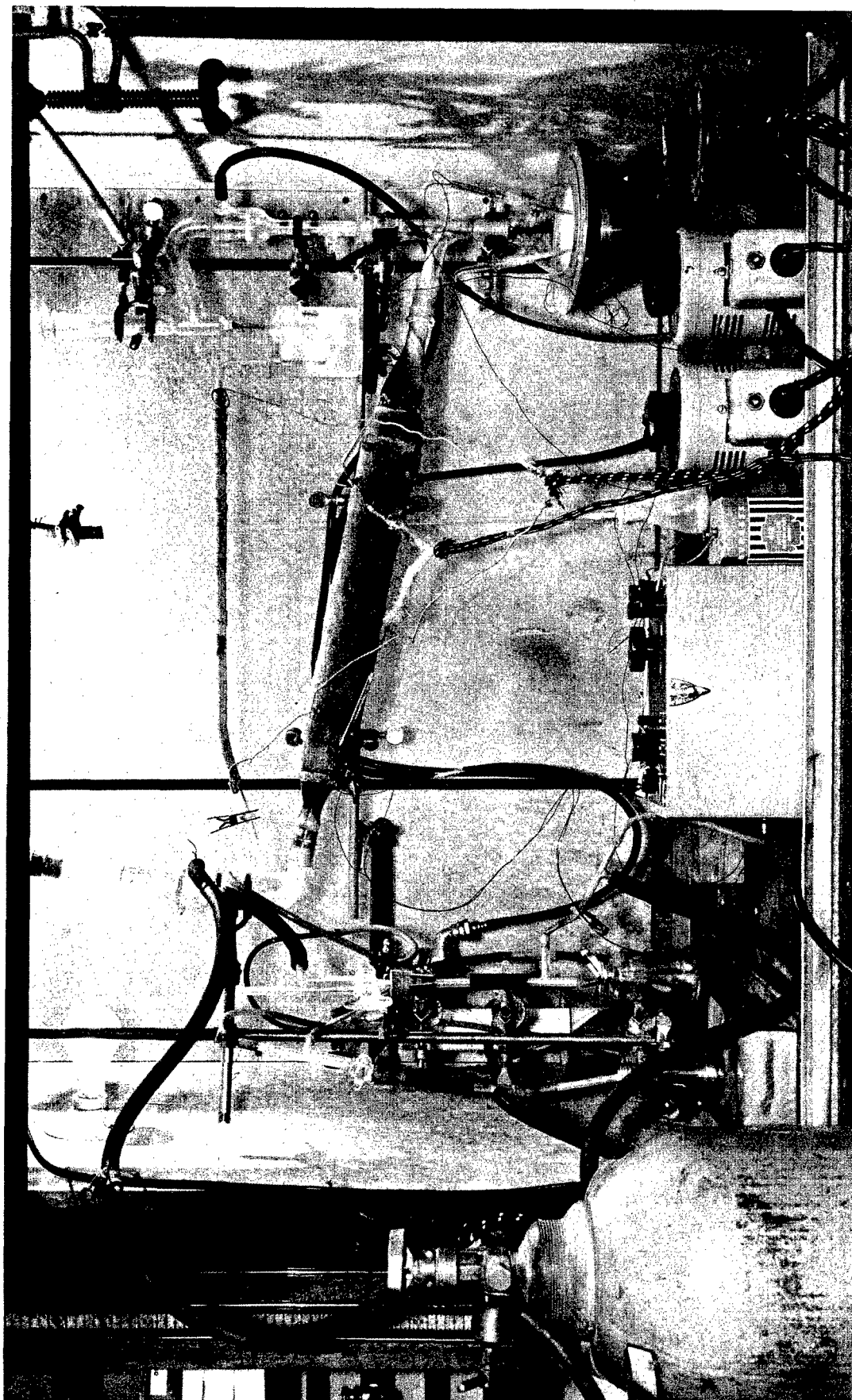


Figure 1 Catalytic Apparatus

The original apparatus had a calibrated dropping funnel for the addition of benzene. Since acetylene is a gas we expected to feed the gas through a short T tube connected to the nitrogen inlet. As will be discussed later, the narrow 8 mm. acetylene-nitrogen inlet tended to clog with crystalline solid material early in the first run. The dropping funnel was then replaced with a 24/40 standard taper joint which was necked down after 10 cm. to 8 mm. size. Most of the solid formation then occurred in the wide curve of the inlet piece and the crystals could be melted by periodically interrupting the flow of acetylene for a few minutes.

The acetylene was obtained from a commercial cylinder of "Prest-O-Lite" acetylene and the traces of acetone removed by the use of a dry-ice cooled trap. Following this trap the gas was dried by passing through a ten inch tower of half inch pieces of fresh calcium carbide. A two way stopcock and mercury regulated overflow allowed for the periodic but not continual measurement of the rate of acetylene or nitrogen gas flows. We are much indebted to Dr. M. W. Leeds of the Air Reduction Company for advice on the handling and purification of acetylene.

2. Preparation of Mercurous Chloride Catalyst

The mercurous chloride catalyst was prepared essentially according to the method described by Arnold (4). Instead of granular carbon we used a special grade of pelleted activated carbon catalyst support low in copper and ash. This was obtained as "Columbia Activated Carbon" Code CXAL-416 from the Carbide and Carbon Chemicals Company. The catalyst was impregnated with a solution of mercuric chloride as described by Arnold but the time of reduction with SO_2 at room temperature cut from 16 to 6 hours. (It is probable that it would be better to use the longer time and perhaps even continue the reduction with the aid of heat and stirring).

The catalyst was pre-dried overnight in a vacuum desiccator and a 360 ml. portion charged in the catalyst tube and baked out under a vacuum of 1 mm. with slowly rising temperature for an hour. At 160° a sublimate appeared. This sublimate may have been unreduced mercuric chloride contained in the catalyst, but this is uncertain. Mercurous chloride also sublimes, but at a somewhat higher temperature than the mercuric salt.

The remainder of the baking was carried out for 4 days at 110° - 120° C.

3. Preparation of β -Chlorovinylboron dichloride

The apparatus was flushed with nitrogen after evacuation and baking and heating to 150° C. The boron trichloride was then fed into the system and the rate adjusted with the needle valve on the tared "lecture" cylinder used. When BCl_3 began to reflux in the dri-ice condenser the flow was reduced and the acetylene stopcock opened gradually. A rate of reflux of at least 1 drop per second of BCl_3 was maintained and normally the rate of reflux and recirculation of excess BCl_3 was about double this rate. A rough calculation based on 1 drop per second gave the figure of 4.29 grams of liquid per minute equivalent to 1.06 liters of gas per minute or 18 ml. per second. This gives a catalyst contact time of 20 seconds with the 360 ml. charge employed. Arnold recommended a contact time of 8-12 seconds and a ratio of 1.5 BCl_3 to 1.0 of acetylene. At this ratio the acetylene feed would be 11.9 ml./second acetylene to 18 ml./second BCl_3 and the combined contact time works out to be about that recommended by Arnold. In actual practice during the major period of the run, the acetylene rate was held between 16.7 and 14.2 ml. per second and the BCl_3 rate at 20-30 ml./second. The run was started at 9:30 but the acetylene was not fed in until 11:15 A.M. The run was closed down at 9:15 P.M. and due to some interruptions the actual running time was 7 hours and 25 minutes. Compensating for caution in increasing the rate of acetylene feed to the stated value this represents about a 7 hour run. The total amount of boron trichloride used was 388.9 g. and the yield of crude product 379.5 g. or about 80% of theory.

During the early part of the run difficulty was encountered in the clogging of the narrow acetylene inlet tube which was obviated by using the wide tube adaptor mentioned earlier. During the run crystalline needles appeared in the gas mixing area and may have been an addition compound of BCl_3 with acetylene. These crystals melted rapidly when the acetylene flow was interrupted in the presence of an excess BCl_3 . In addition to the solid crystal formation there was a certain amount of brown tarry liquid which formed. After five hours tar formation in the fore part of the tube became pronounced and by the next two hours became progressively greater. At the same time the rate of acetylene uptake slowed

to 1.5 ml./second or 10% of the earlier rate. During the course of the run the BCl_3 rate of reflux and recirculation varied from about 1-5 drops per second. The acetylene flow was regulated, after the maximum of about 17 ml./second had been reached, to the rate at which the catalyst could convert the material with practically no excess of gas passing through the end mercury trap.

The temperature of the furnace as measured by the thermocouple averaged 160° with a variation between 150 - 205° C. The conversion rate seemed to be better at the higher temperatures but trouble was experienced with sublimation of mercury chloride at the higher temperatures.

The crude product (379.5 g.) was distilled and owing to clogging of the aspirator some unforeseen losses occurred. The product was 259.5 g. (68.4%) of a light colored liquid, b.p. 55° / 165° mm. or 62° at 220° mm.

The boiling point of the product was constant and the secondary products such as bis-chlorovinylboron monochloride and the tris-chlorovinyl borine were not evident as might be expected from the use of a high BCl_3 - C_2H_2 ratio. A small amount of still residue on hydrolysis gave the impure acid m.p. 121 - 7° .

4. Preparation of β -chlorovinylboronic Acid

Ten ml. of the crude reaction product was hydrolyzed on ice and the crude solid collected. The solid was taken up, treated with charcoal and filtered to remove traces of oil. On cooling, white crystalline plates deposited (3.16 g.) m.p. 127 - 9° with gas evolution and some sintering at 120° .

5. Diethanolamine Ester of β -chlorovinylboronic Acid

Thirty milligrams of β -chlorovinylboronic acid was dissolved in 1 ml. ether and 1 drop of diethanolamine added. The crystals which formed were centrifuged off and washed twice with 2 ml. portions of ether. The product melted at about 219° C. on the Koffler block (decomposition with melting occurred at 204° C.). The lag in the decomposition followed by sudden melting to an oil indicated an organic compound. Also, a few milligrams added to $1/4$ ml. of water formed a clear solution which then gradually gave off bubbles of gas.

6. Preparation of Tri-B-phenylborazole

An abortive attempt was made to prepare tri-B-phenylborazole from the reaction of phenylboron dichloride in ether and the addition of ammonia in saturated ether solution. The only product isolated was phenylboronic acid. Although the ether solution was washed once with dilute sodium hydroxide it seems most probable that the attempt failed due to insufficient drying of the ether and possibly water present in the nitrogen lines. A second attempt using benzene as a solvent was successful and is described in Part III pp. 38-39 (3).

7. Analyses of Tri-B-phenylborazole and Related compounds

Although tri-B-phenylborazole was analyzed and a fairly satisfactory result obtained for boron (Found 10.73 and calc. 10.51%) emphasis was placed on the difficulty of these analyses in Part III, p. 38 (3). With the preparation of a further lot of phenylborazole the analytical problem we re-examined.

The double indicator method of titration with mannitol using methyl red and phenolphthalein tended to give higher results (18.06, 18.01% B in H_3BO_3 with the theory calling for 17.50%) than did the potentiometric titration method following Rieman's procedure (17.45, 17.41% B; all data on aliquots of the same standard boric acid solution.). In the presence of excess peroxide low results were obtained (17.19, 17.19%).

When a 200-300 mg. sample of phenyl borazole was digested first with 5 cc. of concentrated H_2SO_4 with the addition of 1/2 ml. of 30% hydrogen peroxide then made strongly alkaline and digested, further neutralized and titrated potentiometrically low results were obtained (e.g. 8.46, 8.53; theory 10.51%).

This type of procedure was repeated on a very pure sample of the diethanolamine ester of benzeneboronic acid containing a theoretical 5.61% boron. The results ranged from 4.70 to 5.32% B.

8. Preparation of Benzeneboronic Acid

Three runs were made to check the procedure for benzeneboronic acid Part III, p. 23 (3). The results agreed very well

and the yields were 73,65 and 75%.

9. Preparation of Diethanolamine Ester of Benzeneboronic Acid

(a) Run No. 1

Material for a standard analytical sample of the diethanolamine ester of benzeneboronic acid was prepared from 20 grams of recrystallized benzeneboronic acid m.p. 216-18°. The material was dissolved in 25 ml. hot 95% alcohol and 20.1 grams of diethanolamine added. The solution was boiled and crystals separated. An additional amount of 100-120 ml. of alcohol was added with refluxing to dissolve the solid. On cooling about 26 grams (damp weight) of material was filtered off which was recrystallized from 85 cc. of hot 95% alcohol. The material melted at 217.5-219° (3° C./minute) and weighed 21.7 grams. It was marked "standard sample AF14-11-55A".

(b) Run No. 2

A second run of ester was made from 50 grams of benzene boronic acid using a higher ratio of alcohol and yielded 58.5 g. of product and 46.2 g. when recrystallized. From the mother liquor an additional 10 grams was obtained.

10. Preparation of Catalyst for Phenylboron dichloride

A 2% palladium on CXAL charcoal was made in preparation for a run on phenylboron dichloride. It may be noted here that the earlier directions were not too clear on the excess of HCl used in the preparation. According to Hartung's Method (14) each gram of palladium chloride contains 1 gram of palladium and for each gram of palladium an excess of 0.5 grams of HCl or 1.16 ml. of concentrated HCl was used prior to dilution of the palladium chloride solution with 60 ml. of water per gram of palladium. In this and earlier preparations we actually used about 50-100% more HCl than the amount recommended by Hartung. If the palladium chloride solution is evaporated to dryness in a casserole on the water bath and the specified amount of acid is added it is not possible to effect complete solution on the addition of the water. The solution was, therefore, evaporated cautiously on the steam bath to a syrup, the specified amount of HCl added and then diluted with water. Using CXAL pelleted charcoal the reduction

to palladium took place on the charcoal without the need of a reducing agent except when a higher concentration of palladium (10%) or a much higher concentration of HCl was used. (We say reduction of palladium but the reaction may be one of adsorption). Our criterion of complete utilization of the palladium chloride was the lack of color in supernatant liquid and subsequent filtrate.

11. Attempted Large Scale Preparation of Phenylboron dichloride

In Part III (3) we described and illustrated a continuous recirculating apparatus for the preparation of phenylboron dichloride. To scale up the size of runs we constructed a new catalyst chamber of greater capacity than either the original or the later one used for the acetylene reaction (section 1 of this report). The catalyst chamber was made of 52 mm. O.D. pyrex tubing and the wrapping with asbestos paper and insertion of the iron-constantan thermocouple carried out as described earlier. About 62 turns of No. 18 B and S nichrome wire (36.5 feet at 0.419 ohms per foot allowing a current of 7.5 amperes at 115 volts) were wrapped at about one quarter inch spacing over the asbestos covered tube for a length of 15 inches. The furnace in operation gave a temperature of 425° at 98 volts and could be heated to 560° C. at higher voltages. The wrapped and heated section of the tube was 15 inches long and the capacity 625 ml. of charcoal catalyst with 50 ml. of pyrex glass Raschig rings at both ends of the charge. The apparatus is illustrated as Figure 1 of this report, page 13).

As described earlier the 2% palladium on charcoal catalyst charge was baked out under oil pump vacuum (0.1-1 mm.) for 48 hours at 400-450° prior to runs. Operation of the apparatus followed the earlier description but because of the difference in location of the thermocouple and the construction of the furnace (direct wrapped rather than with an air space-outer tube) lower recorded temperatures were used.

An accidental contamination of the catalyst tube and apparatus with mercury while initially being baked out precluded the use of our first batch of catalyst. The entire apparatus was dismantled and each piece cleaned and treated with aqua regia before re-assembling. The results were arbitrarily divided into 3 "runs" but runs 1A and 1B were made with the same catalyst. The separation of product and runs was due to breakage of a part of the apparatus and the product of the

of the first run was analyzed separately. The experimental results are given in Table I.

Table I
Preparation of Phenylboron Dichloride

<u>Run</u>	<u>Product Grams</u>	<u>Percent C₆H₅BCl₂ By Analysis</u>	<u>Calcd. Weight</u>	<u>Benzene Used</u>	<u>BCl₃ Used</u>	<u>Total Time Hours</u>
1A	71.2	30	21.4	88	} 412 g.	21
1B	37.0	-		68		
2	28.0	-		128	179 g.	23
Total: 136.2		64.8	88.3	284	591 g.	17

In run 1A the temperature varied from 300° C. to a maximum of 425°; in run 1B from 400-500° C. and in run 3 from 480-525° C. Due to very poor conversions few conclusions can be drawn as to the yield obtained. Large losses of benzene and BCl₃ were encountered. The first catalyst for run 1A and B was prepared at a time when an accidental influx of H₂S occurred from the adjoining student laboratories and the catalyst may well have been poisoned. Each run was carried out over a period of 3-4 days with a shutdown overnight.

The total crude product from runs 1A, 1B and 2, amounting to 136.2 grams, was distilled at about 75° C. at 30 mm. Due to fluctuations in the vacuum and superheating the distillation range was 65°-85° at 27 mm. The product was probably of better quality than indicated by this range. It has not been re-distilled as yet.

12. Attempted Preparation of Tri-B-β-Chlorovinylborazole in Benzene

The reaction of β-chlorovinylboron dichloride with gaseous ammonia was carried out in benzene and a number of

approximately 20 g. runs (of chloride) were made. In no case was a pure product isolated. The procedure employed was essentially that used for tri-B-phenylborazole and described in Part III, p. 38 (3). For example, a run was made in a nitrogen filled 3 neck, stirred flask in which had been placed 20 grams of β -chlorovinylboron dichloride and 200 grams of benzene. A slow stream of dry ammonia gas was passed above the surface of the stirred solution for 3 hours. At the end of this period excess ammonia was quite apparent in the gas escaping from the mercury trap. Throughout the reaction a slow stream of nitrogen was also maintained to prevent back flow in the mercury trap.

The benzene solution was filtered and washed with benzene. At first the solid was presumed to be ammonium chloride. However, on investigation of this material doubt was raised as to the nature of the solid product. During storage in the desiccator a slow evolution of HCl occurred which obviously could not arise from pure ammonium chloride.

This solid was not completely soluble in water and the residue was insoluble in benzene. About 10% of the "ammonium chloride fraction" was this insoluble material. Extensive fractionation and attempted separations of the insoluble fraction led to inconclusive results since the material appeared to change in its composition during fractionations. Since the original "ammonium chloride" had been thoroughly washed with benzene, the 10% could not be the borazole. However, on extraction of the "ammonium chloride" residue with chloroform a brown product was obtained. This residue on treatment with 6N sodium hydroxide solution gave both acetylene by the Siggia test with ammoniacal silver nitrate and ammonia on testing with litmus paper.

A very considerable effort was expended in attempts to separate and characterize the products in the benzene soluble fraction. In spite of the isolation of crystalline material, presumably impure tri-B- β -chlorovinylborazole, both the solid and the solutions in benzene and other solvents decomposed in two ways. First the slow evolution of HCl indicated gradual decomposition both of the solids and the solutions. Second, during fractionation, particularly in the presence of polar solvents such as acetone, dioxane, and dimethylformamide insoluble materials were formed. In general, the transformation

products were soluble in dimethylformamide. On occasion, some of the products appeared to become partially water soluble. The transformation by polar solvents gave in general products of high decomposition point (above 265° C., the limit of the Kofler hot strip).

The unmodified products melted in the range of 100-125°. Both the original materials, largely the borazole, and the modified products (presumably polymers of considerably higher molecular weight) gave acetylene and ammonia on treatment with 6N alkali. In some cases intermediate molecular weight polymers soluble in dioxane were formed. For example, the benzene solution on freeze-drying gave a dark brownish powder, which partially dissolved in chloroform. The residue, which could not be the borazole, was partially soluble in dioxane and this soluble material gave acetylene and ammonia with alkali.

13. Preparation of Tri-B- β -chlorovinylborazole in Ether

A one liter 3-neck flask was equipped with Tru-Bore stirrer, condenser, addition funnel, gas inlet, and trapped outlet tubes. To 500 ml. of dry ether was added dropwise 26.5 g. of distilled β -chlorovinylboron dichloride with dry-ice acetone cooling of the flask. The addition of the chloride took about 10 minutes and considerable heat was liberated indicating an exothermic reaction probably confirming our initial concept of addition complex formation between the ether and the β -chlorovinylboron dichloride.

A slow stream of dry ammonia gas with some admixed nitrogen was passed over the surface of the stirred ether solution for 2 1/2-hours with continued cooling. At the end of this period excess ammonia was escaping from the trap. Cooling was discontinued and the ether containing suspended ammonium chloride was refluxed for 30 minutes.

The fine slurry was coagulated by the addition of 250 ml. of pentane, filtered and washed with several portions of dry ether. In an earlier run, the ether at this point was evaporated and an attempt made to recover the borazole by distillation but extensive decomposition with the evolution of HCl made further work on the material superfluous. The filtered ether-pentane solution on evaporation in a nitrogen stream gave very fine crystalline needles. Ten grams, or a 70% yield, of

crude product, m.p. 122-5°, was obtained in the first crop.

A number of non-polar solvents were tested for re-crystallizing the material and hexane was selected. The material from hexane melted at 127-128.5° C. (capillary, 3°/min.). Solutions of the purer fractions were reasonably stable on heating up to 100° C. (iso-octane).

14. Chemical and Physical Properties of Tri-B-β-chlorovinylborazole

The crystalline material presumed to be tri-B-β-chlorovinylborazole melted at 127-128.5°. Analytical data are not yet satisfactory. The method for boron analysis has not been adequately studied and standardized. However, alkaline peroxide decomposition followed by electrometric titration in the presence of mannitol gave 11.84, 12.23% against a theoretical boron content of 12.39%. Cryoscopic molecular weight determinations in p-xylene gave variable results, e.g. in 205 and 240, while theory calls for 234.1. Determinations in camphor by the Rast method ranged from 206 to 275. An infrared curve was run but interpretation of the results was not completed.

The material when treated with cold 6N alkali (without the addition of solvent) gave acetylene and ammonia. Attempts were made to run a Kjeldahl type of determination with improvised apparatus but only 74% of theory of NH₃ was recovered. Further analytical data will be required.

The material was soluble in most organic solvents but insoluble or only sparingly soluble in water.

15. Polymerization or Transformation of Tri-B-β-Chlorovinylborazole in Polar Solvents.

The purer material, m.p. 127-8, obtained from the ether reaction was not as sensitive to transformation as the earlier less pure materials.

When the crystalline material was boiled for several hours in benzene or iso-octane practically no change occurred. When refluxed with dioxane no HCl evolution was apparent but a brownish amorphous solid precipitated. This material was

partially soluble in dimethylformamide. It gave a definite positive evolution of both acetylene and ammonia when treated at room temperature with 6N sodium hydroxide solution. The product from the dioxane treatment appeared soluble in acetone in contrast to the earlier products obtained from less pure starting material. Treatment of the purer product with acetone effected a transformation but no acetone insoluble precipitate was formed. On evaporation an oil was obtained which turned to a glassy solid on the addition of hexane and evaporation to dryness. This glass also gave positive tests for acetylene and ammonia with alkali.

16. Analysis of Organo-boron Compounds

Earlier results (see Section 7) indicated that the decomposition of an organo-boron compound with sulfuric acid-peroxide followed by alkaline peroxide digestion gave low results. In a new series of experiments, decomposition of the diethanolamine ester of benzeneboronic acid in 50% sulfuric acid without the addition of peroxide followed by neutralization and alkaline peroxide digestion gave satisfactory results. The 50% acid was used to avoid sulfonation and the formation of an insoluble precipitate.

Procedure: Approximately 100 to 200 mg. samples were digested in a mixture of 5 ml. each of concentrated sulfuric acid and water. The mixture was heated on the steam bath for 15 minutes, cooled, and made strongly alkaline with 6N sodium hydroxide solution. To the solution was added 1.5 ml. of 30% hydrogen peroxide and the whole digested on the steam bath in a 250 ml. beaker for 1 1/2 hours. The solution was then cooled and acidified with 6N hydrochloric acid to pH 3.0 as checked by a Beckman glass electrode pH meter. The acid solution was heated on the steam bath for 20 minutes to expel any CO₂ present and then adjusted to pH 6.3 with standard 0.1 N sodium hydroxide. Mannitol (7 grams per 100 ml. of solution) was then added and the titration continued to pH 6.3. (See references 3,4). The results obtained on the standard diethanolamine ester of benzeneboronic acid were as follows, 5.53, 5.42%; theory is 5.67% boron.

When this procedure was applied to tri-B-phenylborazole the results obtained were 9.22, 9.36, 10.27; the theory 10.51. The results on the borazole still are somewhat low.

Additional work was done on the decomposition of the ester in concentrated sulfuric acid in the presence of added 30% hydrogen peroxide. In all cases the boron determinations were low. For example, digestion to the fuming point of the acid gave 4.64 and 2.75% (theory 5.67%). Comparable amounts of the standard sample when heated in acid on the steam bath gave 5.22 and 4.98%.

Omission of the acid digestion in the case of the analyses of the ester gave quite good results but this probably would not be a suitable method for the analysis of B-substituted borazoles. Results on the diethanolamine ester of benzeneboronic acid essentially following the procedure already described but omitting the acid step gave good results.

On two separate samples 5.64 and 5.59 were obtained. On 10 cc. aliquots of a 1.0929 g. of sample dissolved in 50 ml. of water the results were 5.37, 5.72, and 5.37. In a second aliquot series on a sample of 1.1017 g. the results were 5.37, 5.37. The repetitious nature of the 5.37 result appears wholly fortuitous.

17. Preparation of Tri-B-n-butylborazole

Apparatus. A 2-liter resin kettle carrying a stirrer, gas inlet tube, spiral condenser and a specially constructed 250 ml. addition funnel with provision for evacuation, gas inlet and a mercury bubbler tube, was assembled. A polyethylene gasket was utilized to provide the necessary seal. This apparatus is illustrated as Figure 2 of this report.

Procedure. The whole apparatus was evacuated and flamed thoroughly and then filled with dry nitrogen. Evacuation followed by dry nitrogen filling was repeated three times. With a good stream of dry nitrogen in the system, 750 ml. of sodium-dried ether was charged into the flask and refluxed for 1/2 hour to remove dissolved oxygen. The kettle was then cooled in a large Dewar flask containing a dry ice-acetone mixture.

An ampoule of n-butylboron dichloride was placed in a dry-ice-acetone bath and after thorough cooling quickly opened and capped with a short length of tygon tubing which was closed

with a Hoffman clamp. The tared ampoule was connected through this tubing and another piece of tygon tubing also carrying a Hoffman clamp, to the addition funnel. Air was removed from the major portion of the tubing and the addition funnel, by alternately evacuating and filling with nitrogen. This was done three times. The remaining closed clamp (closest to the ampoule) was then opened and the ampoule inverted. Nitrogen was displaced by opening the mercury bubbler tube as the n-butylboron dichloride was poured into the addition funnel. The ampoule was removed after closing the requisite clamps and then weighed.

A total of 117.5 g. of the n-butylboron dichloride was added to the cold ether within three minutes. A good stream of ammonia was combined with the nitrogen stream and as such passed over the surface of the stirred solution. A white solid presumably ammonium chloride formed immediately. The cooling bath was removed and after a half-hour the ether solution began refluxing from the heat of the reaction. After the beginning of the reaction refluxing ceased. Additional ether (650 ml.) was added in portions to disperse the solid gel which formed and also to replenish the ether which was lost in the nitrogen stream. When a total time of 45 hours had elapsed the very slow ammonia stream was turned off. The mixture was filtered with thorough washing of the kettle and precipitate with dry ether (alcohol free). The clear filtrate was distilled on a steam bath and the ether removed.

About 100 ml. of clear colorless solution remained. This material was warned under aspirator vacuum to remove low boiling materials and then distilled under high vacuum. A total of 51.6 g. for 73% of theory of clear, colorless tri-B-n-butylborazole was obtained in the main fraction, b.p. 80-87° at 97-118 μ , n_D^{25} 1.4494, $n_D^{25.5}$ 1.4492 (original $n_D^{25.5}$ 1.4482).

The final pot residue weighed 5.6 g. and was an amber viscous liquid. Including the weight of the residue in the yield, an 81% yield results.

In a second bulk run 187.0 g. of n-butylboron dichloride was reacted for 21 hours all at dry-ice-acetone temperatures. Working up in the manner previously indicated produced 70.7 g.

or a 63% yield of the tri-n-butylborazole. A residue of 10.0 g. was obtained. If this residue is included, an apparent yield of 72% was obtained.

18. Preparation of Tri-B-n-butyl-N-trimethylborazole

In the apparatus previously developed for the large scale preparation of tri-B-n-butylborazole (See Fig. II) there was placed 1 liter of dry, alcohol free ether. This was refluxed for 1/2 hour under a stream of dry nitrogen to remove all dissolved oxygen. With stirring and cooling in a dry-ice-acetone bath, 250 g. of n-butylboron dichloride was added to the ether while under a blanket of nitrogen. A slight nitrogen pressure was maintained while dry methylamine gas was passed slowly over the surface of the solution. A total of 187 g. of the amine was added over a period of 6-1/2 hours and the whole then allowed to stir overnight. The reaction mixture had gelled and was therefore triturated and refluxed with an additional 500 ml. of dry ether until a workable slurry was obtained. This slurry was filtered and the residue washed by resuspension in dry ether and re-filtration. The combined ether filtrates were distilled to yield an oil. This oil could not be easily rectified by distillation due to the formation of solid which clogged the capillary tube of the still head. Storage of the oil in the refrigerator produced some further solid material.

Part of the original material was treated with hexane in order to isolate further solid material. A small amount of material m.p. 97-103° was isolated.

The major portion of the non-hexane treated when chilled in the ice-box gave only a small amount of solid estimated at 0.2 grams at the air-liquid interface. The product was filtered through a fine fritted glass filter and ampouled by evacuation and sealing off under an atmosphere of nitrogen.

The second fraction which had been hexane treated in an attempt to isolate the solid material was stripped of hexane under oil pump vacuum at 100° C. On cooling and placing in the refrigerator overnight it contained more solid than the earlier sample. Both samples had infrared spectra taken in liquid films (0.025 mm.) and as expected the hexane treated fraction appeared to be less pure.

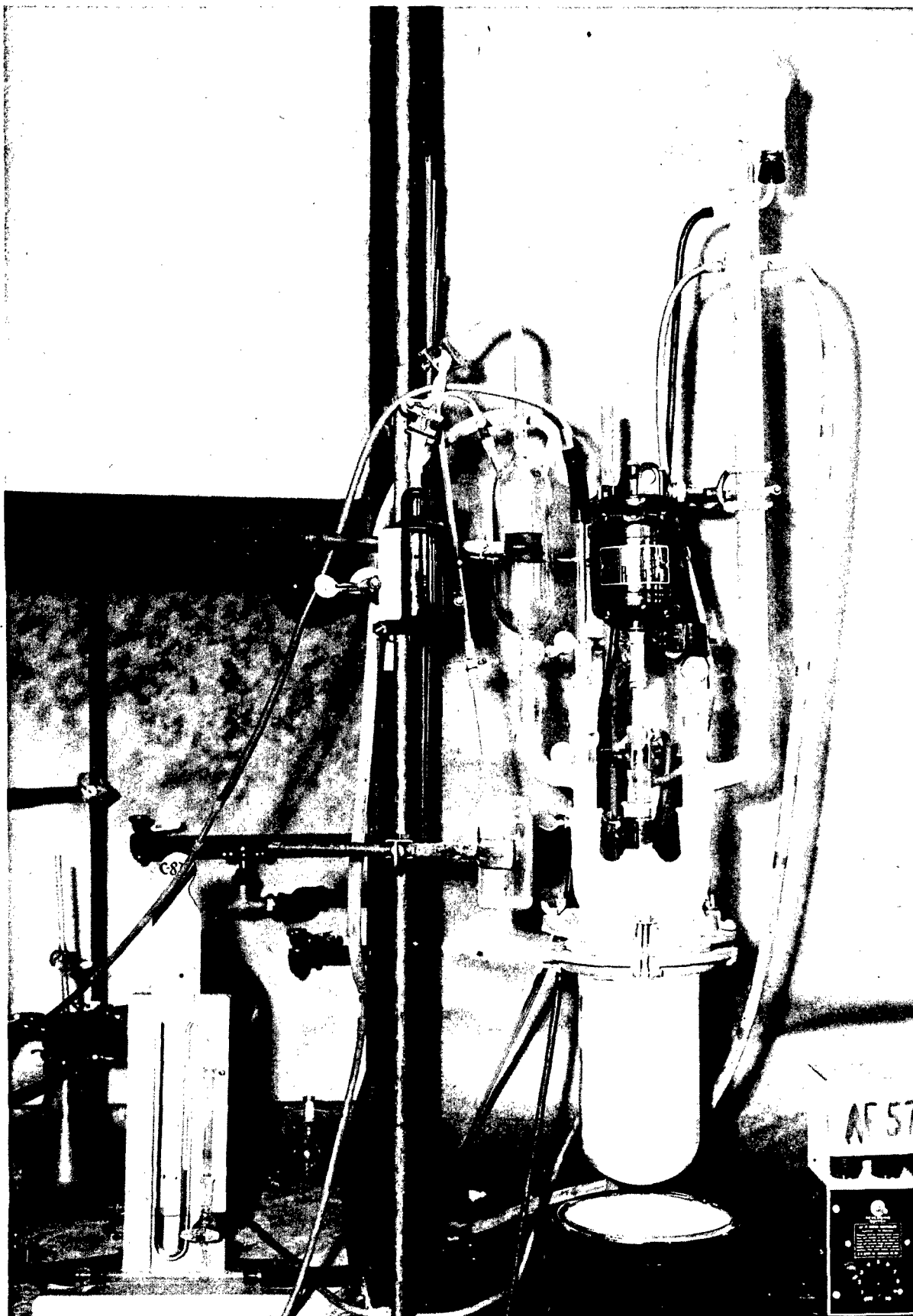


Figure 2 Apparatus for Borazole Synthesis

1st Fraction All-6-56A	76.7 grams
2nd Fraction All-6-56B	<u>27.8</u> grams
Total	104.5 grams

19. Preparation of Hexabutylborazole

The apparatus previously described for the production of borazole from butylboron dichloride and gaseous amines was modified to allow for the addition of liquid n-butylamine. The apparatus was then charged with 1 liter of dry, alcohol free ether which was refluxed under a blanket of nitrogen for 1/2 hour to remove dissolved oxygen. With stirring and cooling in a dry-ice-acetone bath, 190 g. of n-butylboron dichloride was added rapidly to the ether while under a blanket of nitrogen. A total of 302 g. of distilled n-butylamine was added dropwise to the n-butylboron dichloride ether solution over a period of 3 hours. Stirring was continued overnight and the reaction product, which was in the form of a slurry, filtered. The residue was resuspended in ether and filtered and the solid washed on the filter with several portions of ether. A small amount of solid phase appeared in the filtrate and was removed by a second filtration. Concentration of the ether solution produced a viscous amber oil. Distillation under oil pump vacuum yielded a material which partially solidified in the condenser but was easily melted. A total of 124.7 g. or 70% of theory of the hexabutylborazole was obtained, b.p. 90-155° at 100 μ (some superheating).

This material was examined by infrared spectra and compared with the tri-B-n-butylborazole. The NH stretching peak at 3400 cm^{-1} was absent as expected and a slight shift to higher wavelength due to possible resonance appeared in certain areas. The "fingerprint" region had some differences but the spectra were on the whole quite similar.

The material was ampouled by evacuation followed by blanketing with nitrogen. On storage in the refrigerator the sample almost completely solidified in large shining fan-shaped crystals.

AF15-6-56A 118.7 g.

20. Analytical Results on Tri-β-chlorovinylborazole

In section 13 page 22 of this report we described the preparation of Tri-B-chlorovinylborazole in ether, and in section 14, page 23 we gave the boron analyses and molecular weights. In this section we report the micro-analytical results obtained on this material by Mr. J. F. Alicino (P. O. Box 267, Metuchen, N.J.) and two boron determinations done by the alkaline peroxide method in this laboratory (also reported on p. 23).

Anal. Calc'd. for $C_6H_9N_3Cl_3B_3$:

C, 27.51; H, 3.46; N, 16.04; Cl, 40.60; B, 12.39.

Found: C, 27.15; 27.03; H, 3.77, 3.96; N, 15.80, 15.92;
Cl, 40.28, 40.49; B, 11.94, 12.23.

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