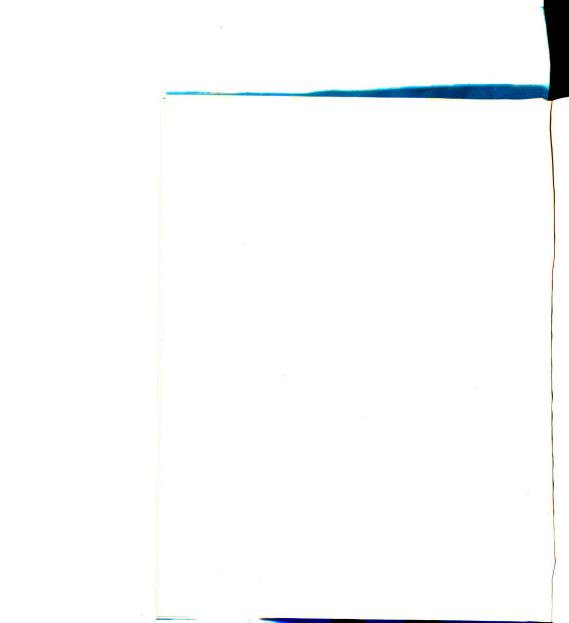
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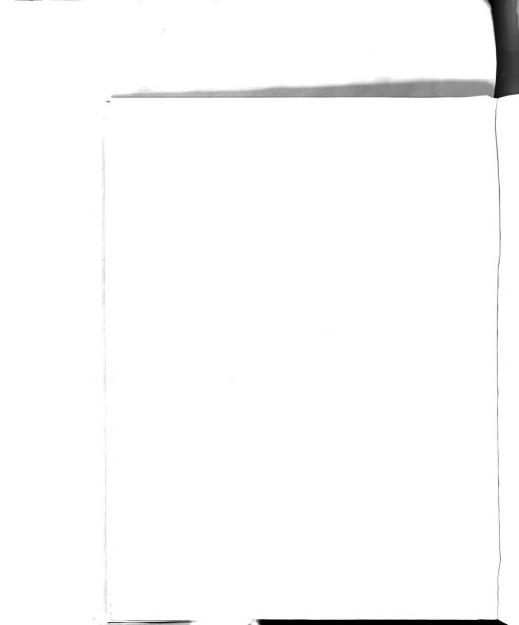
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## PREPARATION AND PROPERTIES OF SOME BOROXINES

By

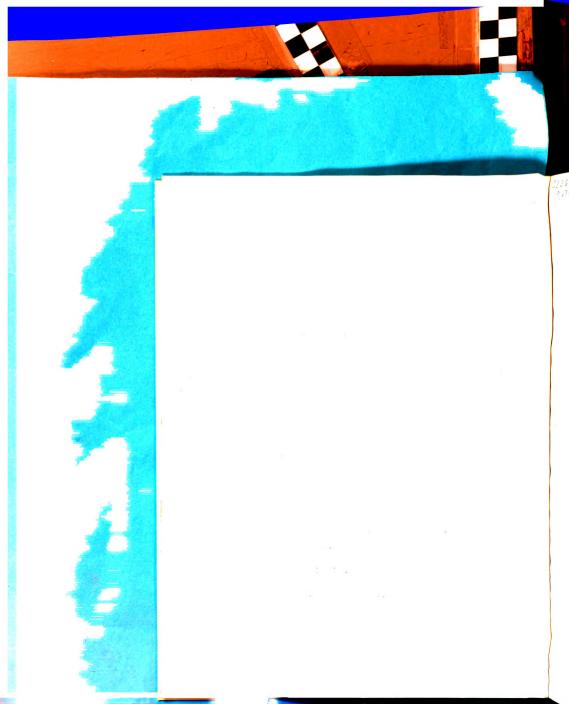
Laurence George Kallander

A THESIS

Submitted to the School of Advanced Graduate Studies of Hichigan State University of Agriculture and Applied Science in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Gremistry





9/27/62

#### ACKNOWL EDGENTS

The author wishes to express his sincere thanks to Dr. Laurence L. Quill, under whose encouragement and helpful guidence this investigation was attempted.

He also appreciates the kind interest and help shown by Dr. William T. Lippincott and others in the Chemistry Department.

The writer is especially appreciative of the graduate teaching assistantships given him by Michigan State University.

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# PREPARATION AND PROPERTIES OF SOME BOROXINES

By

Learence George Kallander

AN ABSTRACT

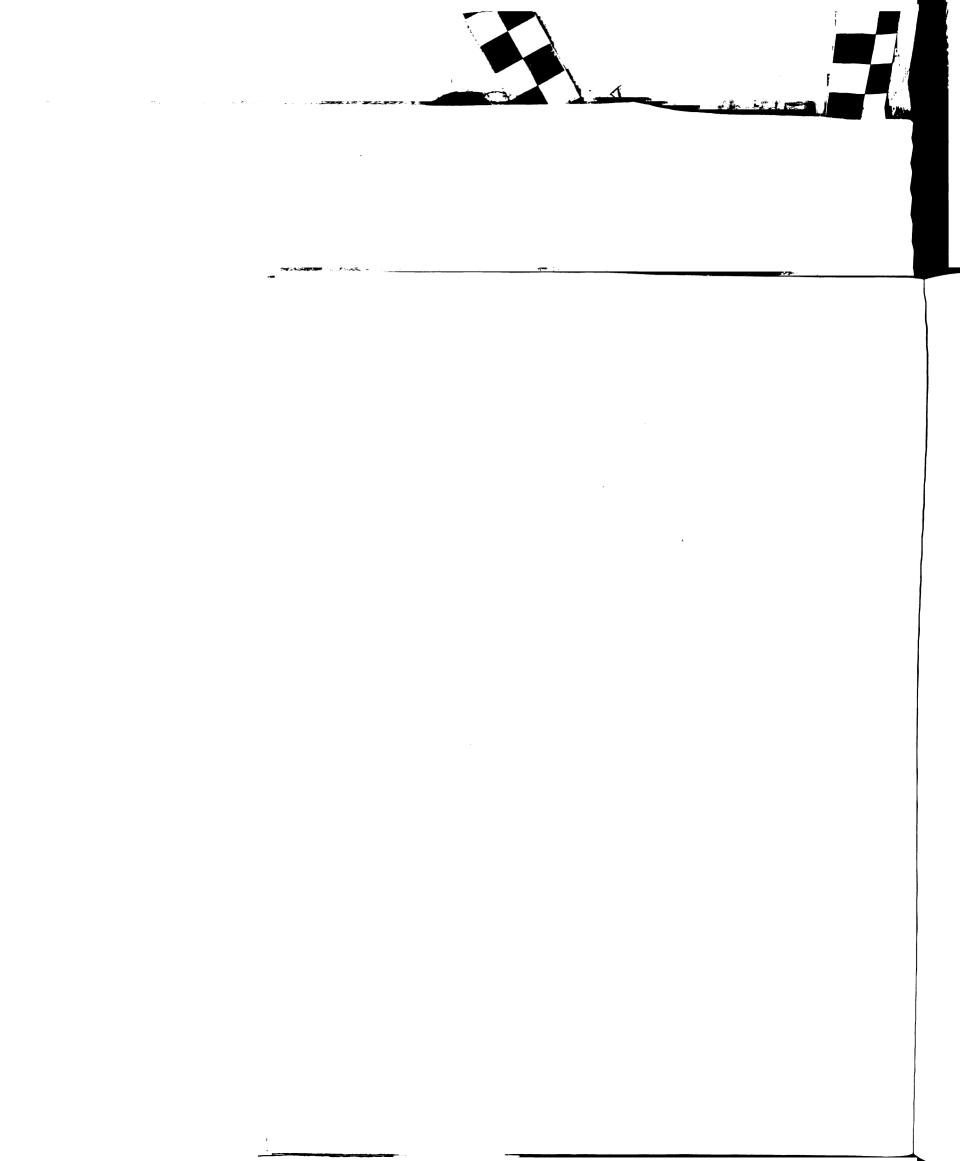
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Year 1959

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#### ADSTRACT

A number of trialkonyboronines were prepared by reacting boron trioxide with the corresponding trialkonyborons. The boronines prepared were triefloxy—, tri-m-propony—, tri-m-butony—, tri-sec-butony—triisobutony—, tri-m-pentony—, tri-m-octony— and tri-m-dodecony—boronine. Except for tri-m-dodeconyboronine which melted at 30° C., the compounds were liquids at room temperature. Of the boronines studied, all decomposed upon attempted distillation to split off the corresponding trialkonyborone. The constitue of the boronines were obtained. Molecular weight determinations and boron analyses showed the compounds to have the trimeric formula (2020)<sub>3</sub>.

Addition of an ether solution of an aniline (aniline, p-caloroaniline, p-emissione, p-nitrospiline, p-aminobensoic acid, p-toluidine,
ani p-aminoacetophenome) to an excess of trimethoxyboroxine in ether
solution at room temperature produced a precipitate which can be
represented by furnature I:

1

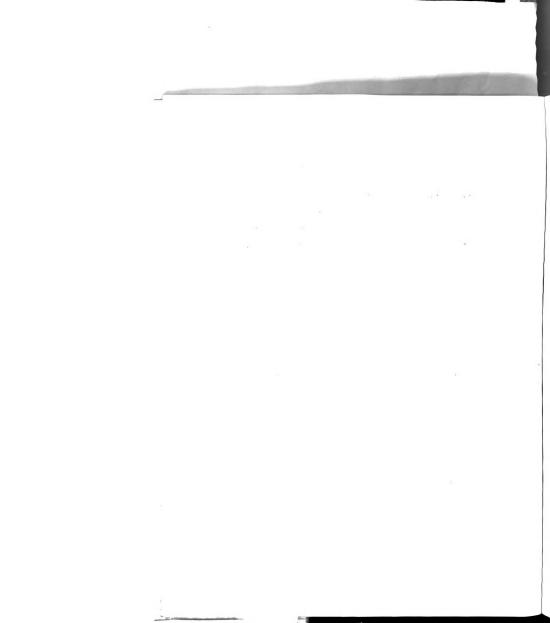


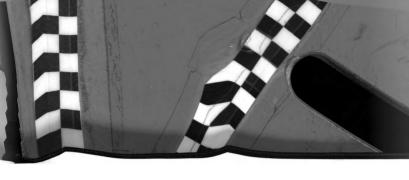
triethoxyboroxine was also successfully used in the reaction, but twi-n-propage, tri-n-butage, tri-sec-butage, triisobutage, tri-npentage, tri-n-octage, and tri-n-dodecoxyboroxine yielded no visible reaction products under identical conditions. The products obtained from the reactions of the diamines, bemidding and phenylenediamine, with tri-methoxyboroxine and triethoxyboroxine are apparently mixtures containing both three and four dialkoxyboroxinyl groups attached to one molecule of the diamine.

Qualike polymers are produced from smiline and trimsthoxyboroxine if the mole ratio of the reactants is near unity and if the reaction mixture is refluxed for several hours. Polymers are also obtained in the absence of a solvent.

Netaboric acid, HBO<sub>20</sub>, was prepared by removal of water from orthoboric acid, H<sub>2</sub>BO<sub>20</sub>, by assotropic drying with toluses or bessen. When sylane was used to assotrope the water, the product had a boron content between metaboric acid and boron tricxide. Experimental evidence indicated that the metaboric acid produced in both the bessens and toluses experiments is HBO<sub>2</sub> III. L-ray powder diagrams are given for orthoboric acid, metaboric acid, boron tricxide, and the sylane dehydration product of orthoboric acid. A comparison of the solubilities of orthoboric acid, metaboric acid, and boron tricxide in a series of alighetic alcohols is given.

Tricyclohomomyboroxine was prepared by the following reactions:
(1) cyclohomomol plus orthoboric acid, (2) cyclohomomol plus astaboric





acid, (3) cyclohemmol plus boron trioxide, (b) tricyclohemocyborene with orthoboric acid, and (5) tricyclohemocyborene with metaboric acid. The reaction of cyclohemmol and tricyclohemocyborene yielded tricyclohemocyborene. The attempted preparation of tricyclohemocyborenies by addition of boron trioxide to tricyclohemocyborene was unsuccessful. All of the above reactions were run with assotropic removal of water by refluxing the mixtures in tolumne.





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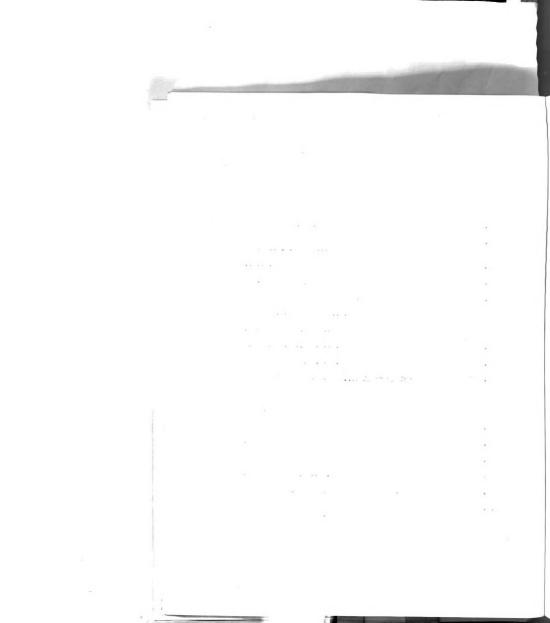
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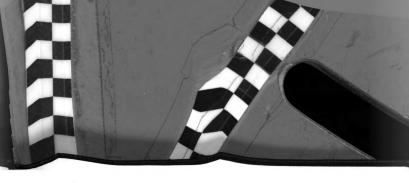
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#### HISTORICAL

For the purpose of more coherent reading, after the Historical, the investigations for this dissertation are grouped into four main elections:

- I. Preparation and Properties of Some Alkonyboroxines
- II. Reaction of Aromatic Amines with Alkonyboronines
- III. Dehydration of Orthoboric Acid
  - IV. Tricyclohexoxyboroxine

Each of these four sections is divided into three topics: Introduction, Experimental, and Discussion. These four sections are followed by a Summary of the entire thesis study. Lastly, there is a discussion of Future Experimental Problems.

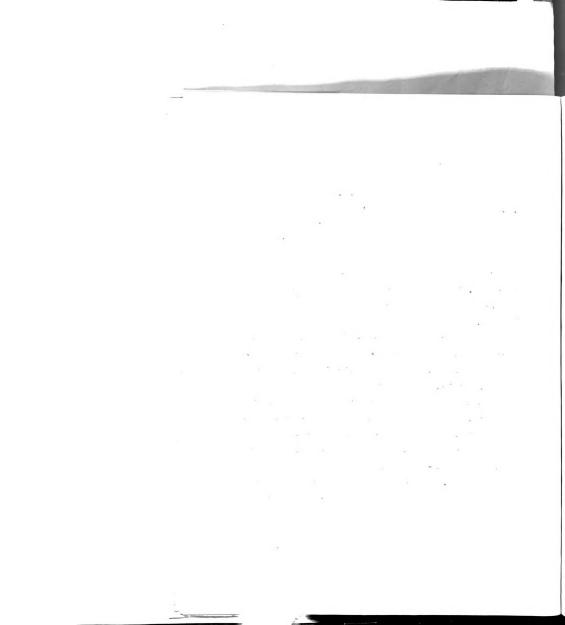
The growing interest in boron chemistry has been highlighted by the many recent newspaper and nonscientific journal articles dealing primarily with the use of boron compounds as fuels. Studies of many outstanding chemists, such as, Schlesinger, Burg, Parry, Goubeau, and Wiberg, are noted in the several reviews no boron chemistry that have been written in the last few years (1,2,3). That the chemistry of boron can no longer be classified exclusively as inorganic chamistry is exemplified by Lappert's extensive review on organic compounds of boron (h).

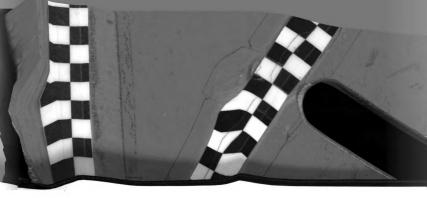


In recent years, investigations on the preparation and properties of boron hydrides were made in this laboratory at Michigan State
University under the guidance of Doctors L. L. Quill, D. T. Bring, and
R. K. Birdwhistel. Included were Ulmer's study on the electrolysis of
oxygenated boron-containing materials (5), Johnson's study on the gaseous
diffusion of diborane, hydrogen, and nitrogen (6), and Ogle's study on
the production of reduced boron compounds and boron hydrides (7).
In Ogle's work some properties of trinsthony- and tri-n-butoxyboroxine
were studied. It was the purpose of this present investigation to
prepare additional alkoxyboroxines and study their chemical and physical
properties.

2

A survey of the literature of boron-coyen compounds reveals a variety of nomenclatures for the six-membered ring systems of alternate boron and coyen atoms. Boric acid subpdrides, boronic subpdrides, boronics, boroxines, metaborate, metaborate trimers, metaboric acid esters, metaboracetates, organoboron oxides, trialityl triborance, tricumes, and triboron coyhalides have been used by various investigators to describe the shows-mentioned compounds. The term "boroxole" was ascribed to these compounds by Wiberg (8,9) in enalogy to the borosoles, the six-membered ring compounds containing alternate boron and nitrogen atoms. Hore recently Schaeffer and Wartig (10) proposed a nomenclature for boron compounds in which the six-membered ring systems consisting of alternate boron and oxygen atoms are called boroxines. The three swallable positions for substitution in the boroxine ring are designated by numbering in a clockwise direction, beginning with oxygen.





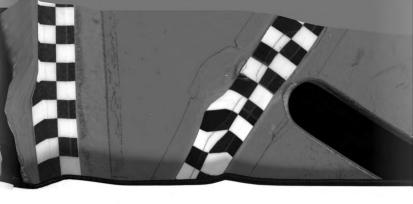
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Time, by the system of Schaeffer and Wartig, (BOF)2(I), (GH2BO)2(II), and (GiaGBO)a(III) would be

named 2,4,6-trifluoroboromine; 2,4,6-trimethylboromine; and 2,4,6-trimethogyboroxine, respectively. Current papers appear to follow this system, with the modification that the numbering system has not been used, since all such compounds reported have been symmetrical. The term "boroxine" will be used throughout the remainder of this thesis, except when mention is made to literature in which the boroxine was originally given a different name.

Since this investigation is primarily concerned with boroxines of the general formula (RCBO) , where R is an organic redical, this type will be reviewed first. These compounds are often called metaborates, since they are esters of astaboric acid HOBO, and have a formula similar to the inorganic metaborates, e.g., (NaBOn), and (KBOn), (10,11).

Schiff (13) found that boron trioxide dissolved in the trimethyl and triethyl esters of orthoboric sold to form metaboric sold esters according to the equation



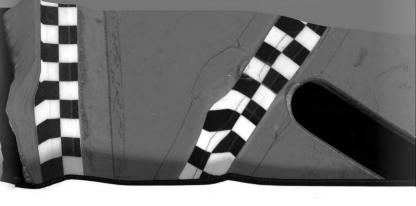
ghiv. metaborate was also drtained by Schiff from etherol and boron terioscide as follows:

In the same study the metaborates were also obtained by the treatment of the orthoborates with borde acid. Schiff found sthyl metaborate to be a syrupy hygroscopic liquid which decomposed upon heating and reacted with ethanol to form tricthyl borate.

Hethyl neteborate, (GioGO)<sub>x</sub>, was presumed by Schlesinger and coworkers (lk) to be present as the gamp residue in the preparation of methyl borate from methanol and boric oxide. Similarly, a product (probably metaboric ester) which decomposed during distillation was obtained by Stridge and Sugien (15) when an excess of boric anhydride was used in the reaction with methyl sloohol and ethyl alcohol in the preparation of the corresponding orthoborates.

The first study of the properties of trimsthoxyboracols was carried on by Goubean and Keller (16), who prepared the compounds by a modification of the procedure of Schiff (13), using boron trimside and the trimsthyl ester of boric acid. These investigators found trimsthoxyloracols to be trimsric (cryoscopic and sbullioscopic in beamens). The compound from at approximately  $-10^\circ$  and decomposed above  $170^\circ$  into the starting materials. Ranan spectra of trimsthoxyboracols has been reported by Goubeau and Keller (17) to give proof for a six-membered  $B_0 C_0$  ring. Ogle (7) prepared trimsthoxyboracine by the method of Goubeau





and Keller (16), confirmed the trimeric nature (cryoscopic) in beasens, and obtained the infrared spectrum, the density, and the vapor pressure. From the vapor pressure data, Ogle calculated the boiling point, the heat of vaporisation, and Trouton's constant for trimethosphorazine.

5

The above-mentioned data conflicts with a recent study by Carpenter, Rughes, and Bargman (18) on the preparation, properties, and structure of trimethoxyboroxines. This paper reports that the system methyl borate-boron trioxide actually contains a variety of polymeric boron oxides, linear, cyclic, and cross linked, which are substituted to various degrees with methoxy groups. The system was studied from 0-71.5% boron trioxide. Infrared and Ream spectroscopy failed to confirm the predominance of the cyclic structure previously reported. The variations of the following physical properties with the ratio of methyl borate to boron trioxide were studied by the same investigators; apparent nolecular weight, boiling point, freezing point, viscosity, refractive index, density, dialectric constant, and conductivity. Examination of these data showed a continuously varying composition rether than a solution of (Gi<sub>2</sub>GBO)<sub>3</sub> in the emoses component.

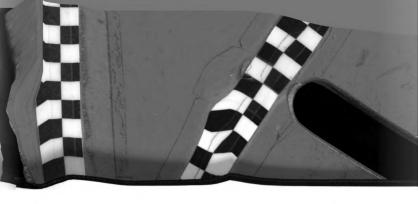
Povlock (19) reacted trimethoxyboracine with anylgrigants in the preparation of anylboranous acids. The yields were much greater than those obtained by carlier asthods.

Hetaboroscetate, BO<sub>B</sub>ie, is mentioned by Dimroth (20) as the product when scetic embydride is split off by heating pyroboroscetate,  $B_BOAc_{\phi}$ , at 150-60°. Crystallisation from scetic embydride regenerates pyroboroscetate.

seed Markey (16), castificant the trabaltet category (veycampto) in become erinancing today old has arthured operation, the departity, and the vence presented from the vegor presency date, being colorabled the bolling point; the house of vegoriantion, and theological according that tollighteen and fundamental and which thereon is also allele alleles beautique-woods and Hughes, and Engyan (28) on the propertion, properties, and standour educated Dutties and age told david servers toward that age ton age ton accept because bower textenide controlly contains a variety of polynaria boxes unidanced Money cyclic, end arone Linked, which are maketikeded to variets degrees with spinory groups. To system me started from U-71.55 bozon triuride. the secretary and secretary and the confirm the predominance of the galantich edt in antiekter och . Dersonst glesekven enstende akteu stimulated strong of extend figures to other wer dates so have property furthering publish delphus valueales decreep, terodestiments come ed yd bolishe even poleti, freezing polet, visconity, refrective lenter, density, dishertante complete, and contentiality. Emplanifier of these data discusses as confused and at a(OND, an existing a main resist relation of (display) at the . Ammorphie deletes

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intobarcacebake, bo<sub>s</sub>ho, is mediamed by Lievach (20) on the preduct when eastle respirate is split off by housing symboroscotting, hydrig, as 150-60°. Crymbolitzation from actific comparation regressmokes pyrobacecacebake.



The melting point for isopropylmetaborate ester is listed as 17-59° by United States Borez and Chemical Corporation (21).

Tri-n-butoxyborazine was prepared by Ogle (7) by reacting diboron trickide with tri-n-butoxyborane. Ogle showed by molecular weight determination (cryoscopic in beasone) that this occapand is a trimer. The tri-n-butoxyboroxine decomposed when distilled and froze into a glass-like solid at -75°. The densities at various temperatures, along with a few pressure values, were determined. The infrared spectrum was also ascertained by the same investigator.

The density of n-butyl metaborate ester is listed on a technical data sheet of United States Borax and Chemical Componetion (21).

Oxidation of n-butyl boron oxide was found by Grunnitt (22) to proceed quantitatively seconding to the equation

the product being the n-butyl ester of metaboric soid. The n-butyl metaborate thus prepared was reported to be measurate (oxycscopic in bemsens).

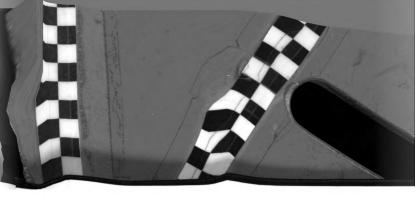
O'Commor and Nace (23) attempted to prepare n-butyl metaborate acid by esterification of boris acid with an equincler quantity of n-butenol and assotropic removal of the water formed with toluene. The n-butyl metaborate could not be obtained pure, however, since it decomposed to n-butyl borate upon vacuum distillation.

A substance which appeared to be related to the trimethoxyboroxole described by Goubeau and Keller (16) was produced when O'Brien (24) Med-a-babageouslas vas projected by Ogla (7) by resolving this and this as a finishe with the network by Ogla (7) by resolving this collection with the network of the first programming the babage, as absentional conference of the first programming the absence of the first projection and the second training the first projection to the first programming along the first programming the first prog

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attempted to prepare tri-t-butyl borate by the assetrope method, using t-butsmol, boric soid, and bensene.

When 0°Comnor and Nace (23) heated equimolar quantities of 1-menthol or cyclohecanol and boric acid under reflux in toluene two molar equivalents of water were formed and the respective metaborates were obtained in practically quantitative yields.

Notecular weight determinations showed the compounds to be trimere. Pyrolysis at  $270^{\circ}$  of 1-mentical metaborate trimer (m.p.  $133-15^{\circ}$ ) and cyclohexel metaborate trimer (m.p.  $165-67^{\circ}$ ) yielded methens and cyclohexens respectively. L-Menthyl metaborate trimer was found to hydrolyse to 1-menthocyboric acid,  $ROB(CE)_{2}$ , in moist air.

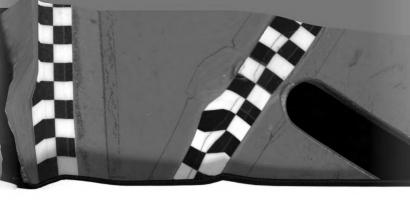
In this present thesis study, a number of trialkoxyboroxines (trinsthoxy-, tristhoxy, tri-n-propoxy-, tri-n-butoxy-, tri-sec-butoxy-, tri-iso-butoxy-, tri-n-pentoxy-, tri-n-cetoxy-, and tri-n-dedecoxyboroxine) were prepared by reacting boric ampricide and the corresponding alkyl orthoborate. Since the completion of this author's experimental work, Leppert (25) has published an article on the preparation of sethyl-, ethyl-, n-propyl-, isopropyl-, n-butyl-, isobutyl-, and sec-butyl metaborate by decomposition of the corresponding dialkylchloroboromate either under reflux for a stated time or by adding a catalyst. The above mentioned alkyl netaborates and phenyl metaborate were also prepared by Lappert (25) by heating a mixture of the orthoborate (1 mole) and boron trioxide (slightly > 1 mole). Purification of the metaborate was

attached to propose tele-beigh bearis by the enothers settled, uning

These of Courses and State (5) listed and included quantities of I-continue or synthemental and burdle could under retain to believe the solution that solution and shelled in respectively and the two years.

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was prepared by reacting boats saightful and the corresponding slags
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antificient allocation and planed introduction were also prepared by
Lappent (25) by heating a sintens of the extinction were also prepared by
thinds (slaghtly > 1 miss). Trustination of the meliconte was



affected by dissolving the product in a large volume of an inert anhydrous solvent, filtering, and evaporating the filtrate under reduced pressure. The infrared spectra and indices of refraction of the notaborates were obtained by Lappert (25) who also reported that attempted distillation of the netaborates under reduced pressure caused decomposition to yield the orthoborate and boron tricaids.

8

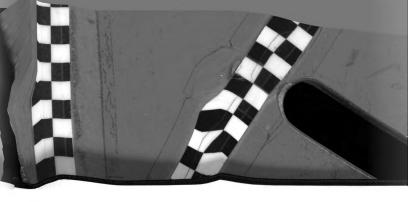
The largest group of boroxines is the one in which the R in (REO)<sub>3</sub> is an alkyl or snyl group. These compounds are often called boronic anhydrides, since they are usually prepared by the dehydration of a boronic soid, RE(CH)<sub>2</sub>. The reaction

has been carried out both by thermal means and by the use of dehydrating agents. The alicyl and anyl berowines are more numerous in the literature than the alicny and anylony berowines. This is probably due to the fact that unlike the latter, the former may be purified by distillation without decomposition and the parent berowic acids are available. The fact that the compounds  $BC(W)_2$ , from which the anhydrides  $(BO)_3$  are prepared, are comen, whereas there is only one case of a compound  $RCB(W)_2$  being reported (23), because more interesting if one views the "parent" compounds, RCBO and RBO. Metaboric acid, RCBO, is well-known (1 mole orthoboric acid, BCBO, mixes 1 mole BCBO equals 1 mole metaboric acid, BCBO). However, the "parent" compound BCBO has never been isolated. Attempts by Burg (26) to prepare this acid by reacting

ationing by discripting the province in a large value, of an insert
entrance entrent, filtering, and other making the Illiance-anion reduced
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trimsthyl boroxole with diborane,  $B_2H_3$  or boroxole,  $H_3B_3H_4$ , were not successful. Ogle (7) studied the reaction of trimsthoxyboroxine with sodium hydride, but did not obtain the desired HBO.

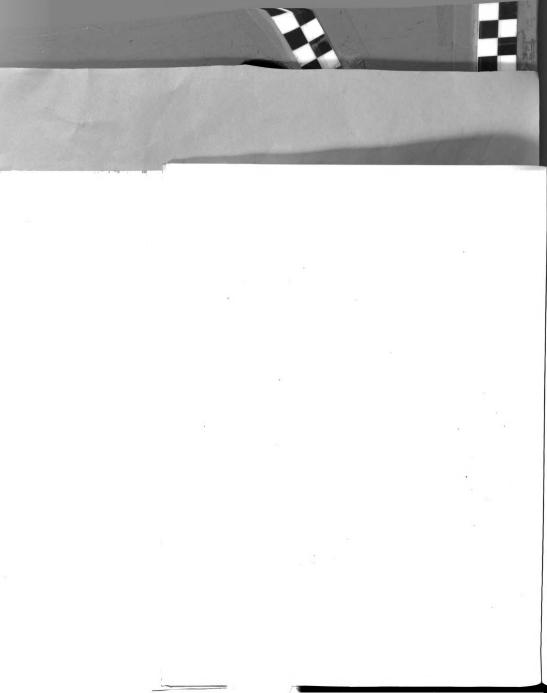
9

Leppert (h), in an extensive review of organic compounds of boron, lists a table of physical constants of boronic ambydrides which is reprinted below with additions and corrections. A survey of the literature, however, indicated that in many cases the boroxine was not positively identified by chemical analyses nor molecular weight determinations.

Eass a more thorough description of the preparation, identification, and properties of the aligh and anyl boroxines will be given.

The question that the boroxines might not be monomeric arose from a study by Kinney and Ponts (27) on the molecular weights of the organo-boric soids. An examination by those investigators of the data demonstrated that the organoboric soids studied do not associate in nitrobensens and that in this solvent there is no appreciable amount of hydrogen bond formation. Preliminary experiments in the same study showed that these substances have a tendency to dehydrate under the atmospheric conditions prevailing in Sait Lake City and that the products have high molecular weights. Derivatives of boric soid studied were:

Phenylp-Tolyln-Chlorophenylp-Chlorophenylp-Bronophenylo-Phenotylp-Phenotylo-Haphtbyl-



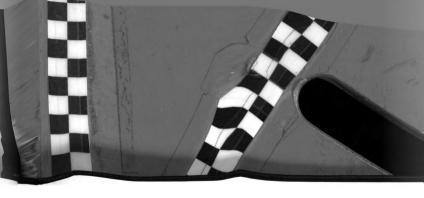
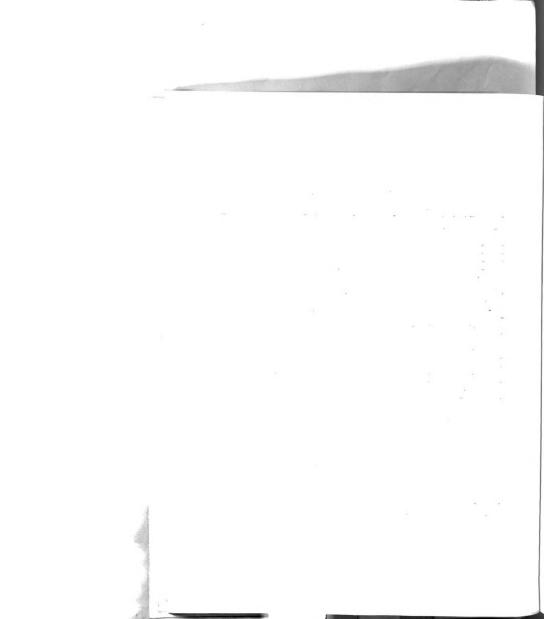


TABLE 1
PHYSICAL CONSTANTS OF BORONIC ANATORIDES

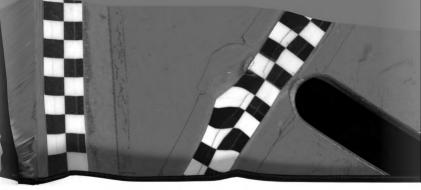
R in (RBO)3	Melting Point	Boiling Point	References
Cligo n=C <sub>2</sub> ligo	-38	79	16,17,26,30,31,32 33
n=C <sub>a</sub> li <sub>y</sub> = n=C <sub>a</sub> li <sub>0</sub> = i=C <sub>a</sub> li <sub>0</sub> =		138/18 mm.	22,28,29,33,35,36,37,38,39,14
to Callon no Callago		66-68/5 m.	10,12 37,38 31
to CoH2200		11.9/5 mm.	3h 29
GE 11"	211-216		27,28,34,41,42,43,44,47
colistala colistala	160-161 160-161.5 259-260		45,47 47 27,28,47,49
o-Clodig OdigClig O-Clodig	140 167-169		51 50
m-ClC-H4-	178-179 211-262.5		27,28,47 27,28,47
p-BrCdla- p-GH30Cdla-	301-302		27,28,47,48,49
m-CH <sub>2</sub> OC <sub>2</sub> H <sub>4</sub> -	159		50 50 50 27
p=C <sub>2</sub> H <sub>3</sub> OC <sub>3</sub> H <sub>4</sub> = c=C <sub>2</sub> H <sub>3</sub> OC <sub>3</sub> H <sub>4</sub> =	171		50 27
o-OgliColia- m-OgliColia-	280-281 285-286		52,53 17,53
m-C <sub>2</sub> H <sub>0</sub> 00CC <sub>0</sub> H <sub>4</sub> p-C <sub>2</sub> H <sub>0</sub> 00CC <sub>0</sub> H <sub>4</sub>	- 198-200		72
o-CallaCalla- 2,h-(Clia)aCall	195 s- 202		16 16 17
3,µ~(CH <sub>3</sub> ), <sub>2</sub> C <sub>d</sub> H 2,5~(CH <sub>3</sub> ), <sub>2</sub> C <sub>d</sub> H <b>2</b> ,5~(CH <sub>3</sub> ), <sub>2</sub> C <sub>d</sub> H <b>2</b> ,0C <sub>d</sub> H <sub>3</sub> OC <sub>d</sub> H <sub>3</sub> ~	3- 226 3- 176	,	146 27
G=G <sub>10</sub> Hy=	207		27,28,45,49





Kinney and Ponts (28) then made an investigation of the structure of the organoboron orides. The oxides were prepared by heating the corresponding boric acid derivative for 33 hours in a drying oven held at 110° C. The products were then analyzed for boron and their molecular weights determined cryceoppically in mitrobensons. A consideration of the data showed that the organoboron oxides cannot have the simple formula 880. Kinney and Ponts deduced that the variations in the values for duplicate molecular weight determinations probably indicate that mixtures of double, triple, and perhaps higher molecular weights are produced. The same investigators made a comparison of the structure of the exides to that of boron exide (boric ambydride) in which at least one oxygen bridge (OBCBO) must be present. They said that since boron oxide as ordinarily prepared is a glass, it is likely that it has a molecular weight higher than boric oxide and that a number of boron atoms are linked together through crygen atoms. This comparison led Kinney and Pontz to suggest the formulas below rather than marely associated molecules

The trimeric formula was adjudged to be similar to those accepted for the trimers of the aldehydes, thicaldehydes, and thicketones. Derivatives of boron codds studied by Kirney and Ponts were:

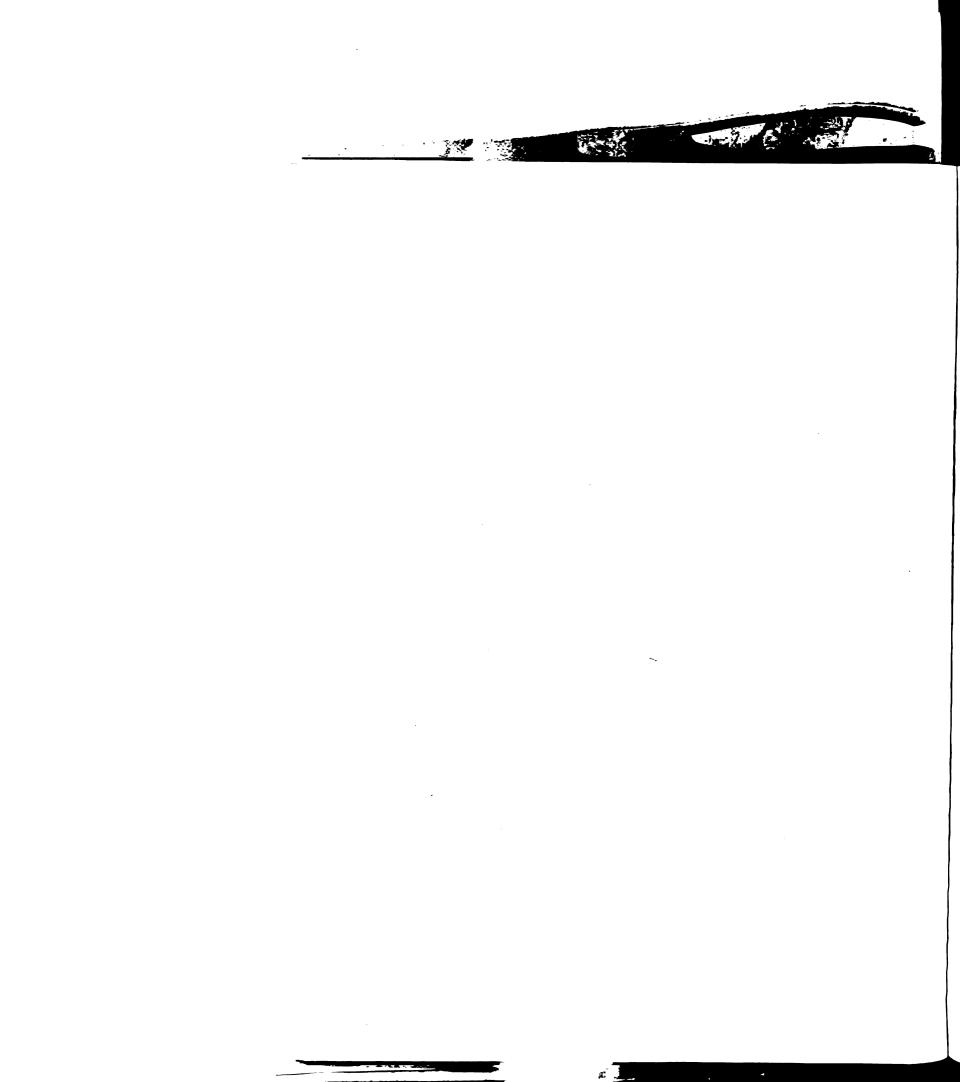


Phenylp-Tolylm-Chlorophenylp-Chlorophenylp-Brosophenylc-Hophthyl-

A further suggestion on the structure of boron oxides was made by Snyder, Knok, and Johnson (29) after obtaining molecular weight data showing n-butylboric oxide to be trimeric. These authors suggested a cyclic structure analogous to alighatic aldebydes and furthered this view by the observation that the bodling point of n-butylboric oxide is close to that of the corresponding paraldebyde homolog. It was noted by the same investigators that the relatively great stability of the cyclic trimers may be due in part to resonance offects involving an unshared electron pair of the open sexted of the 3-covalent boron.

The lowest member of the allyl boronine, trimethyl boronine, has been prepared by various methods. As is the usual case with the first of a homologous series, this boronine has undergone a more complete study than many of the others.

Burg (26) first prepared nethylboric subviride by sublinding nethylboric acid through anhydrous calcium sulfate in a vacuum system. The molecular weight of the compound, obtained by Burg by vapor pressure measurements, showed the compound to be a trimer, (GigBO)<sub>2</sub>. The heat of



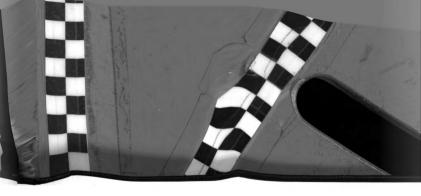
9.

13

reportsation and Trouton's constant were calculated. The anhydride formed a monotrinsthylaminate, a mono-ammoniate and a far less-stable diamoniate; from the data Burg concluded that only one boron atom (of the three in the ring) can co-ordinate with an electron-donor atom. The same investigator found that the ring of methylboric anhydride is split by the action of boron trifluoride, to form methylboron difluoride, Chapte in excellent yields.

An electron diffraction investigation of trinsthyl triborine tricuone, (Gi<sub>2</sub>BO)<sub>3</sub>, by Bauer and Boach (30), lead to the following structures planar six-membered ring with alternating boron and oxygen atoms, with the methyl groups bonded to the boron atoms and in the plane of the ring. Values for the B-O bond, B-C bond, and B-O-B angle are given by these authors.

Wibers and co-workers (31,32) prepared trimethyl bereacle by partial hydrolysis of p-trimethyl beresole and hexamethyl bereacle with three moles of water



The addition of excess water gave mothylboric acid and amnonia or methyl amine, respectively.

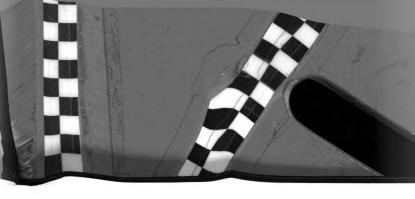
Trinsthylboroxole was formed by Goubean and Keller (16) from the compound, boric oxide,  $B_2O_3$ , and trinsthyl borines,  $B(Gi_3)_3$ , at 300-330°C. and 15-20 atm. in a 6 hour reaction.

It formed a water-clear liquid which in hund air hydrolysed slowly to form nice crystals of methylboric acid. Vapor pressure measurements showed the compound to be a trimer. Reman spectra by Goubsen and Keller (17) confirmed the trimeric nature of the trimethylborocole.

In a recent study Keller and Perrins (33) reported that ethylboromic acid,  $C_2H_0B(GL)_2$ , could not be dehydrated to ethylboromine,  $(C_2H_0BO)_3$ . The same paper reports the preparation of ethylboromine by the thermal decomposition of butylboromine above  $700^{\circ}C$ .

Krause and Mitsche (34) emanined a number of trialkylborines (n-propyl, isobutyl, and isosmyl) and concluded that the normal autooxidation (controlled by slow admission of air) gives rise to estaws of
the alighstic boronic soids or to the alkylboron oxides. They did not
isolate and identify these products but showed that the alkaneboronic
acids were produced upon hydrolysis. In a later study by Johnson and
Van Campen (35) on the autooxidation of tri-n-butylborine, the formation
of the alkylboron oxides, reported by Krause and Mitsche was attributed
to hydrolysis of the estar by a limited amount of water (atmospheric

3 . c



### noisture) after the initial oxidations

Snyder, Ruck, and Johnson (29) prepared n-butylboron oxide (1-butane-boronic ambydride) by heating n-butyl boronic acid under reduced pressure or by summing the acid with thionyl chloride. The trimeric exide formed uses identified by chemical analysis and nolecular weight determinations. These investigators found that the oxide reacted with water to regenerate the acid. When ambydrous amonia was bubbled into a solution of the exide in dry other, a white crystalline precipitate was formed. Heat was generated when the oxide was added to phenylhydrasine, antline, methylamine, dimethylamine, disthylamine, tricthylamine, dimethylamine, and tri-n-butylamine, but a solid was not obtained in any case.

Treatment of an ethereal solution of the ambydride at -65° with a considerable excess of n-butylampersium bronde gave a small quantity of tri-n-butylborine, but most of the material was recovered after hydrolysis as 1-butaneboric acid. The n-butylboron oxide was identified by chemical analyses and molecular weight determinations (sbullioscopic in beaucone).

Dworkin and Van Artedelon (36) studied the molar heats of solution of n-butylboric sold and tri-n-butyl boric oxide. Their results were summarised by the following equations:

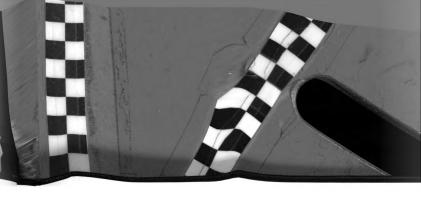


3. 
$$(C_4H_0BO)_2$$
 (1) +  $3H_2O \longrightarrow 3$   $C_4H_0B(OH)_2$  (c)  
 $\triangle H = -19.6 \pm 0.04$  Real

Grunditt (22) found that n-butylboron oxide undergoes quantitative oxidation and depolymerisation in the presence of dry oxygen to form monomeric n-butyl metaborate. There was evidence for the intermediate formation of a peroxidic substance. The following reaction mechanism was suggested by Grunditt, but could not be confirmed by rate measurements because the kinetics were complex.

Glams (37) prepared trimeric n-butyl boron oxide, n-anyl boron oxide, and n-haryl boron oxide by the nothed of Snyder, Ruck, and Johnson (29), utilizing thionyl chloride to dehydrate the respective allylboronic acids. For n-butyl boron oxide and n-anyl boron oxide, he determined the infrared spectra and detarmined the densities and refractive indices. HeOusker and Glams (36) confirmed the stoichionstry of the reaction of boron fluoride with alkyl boron oxides first proposed by Burg and represented by the equation

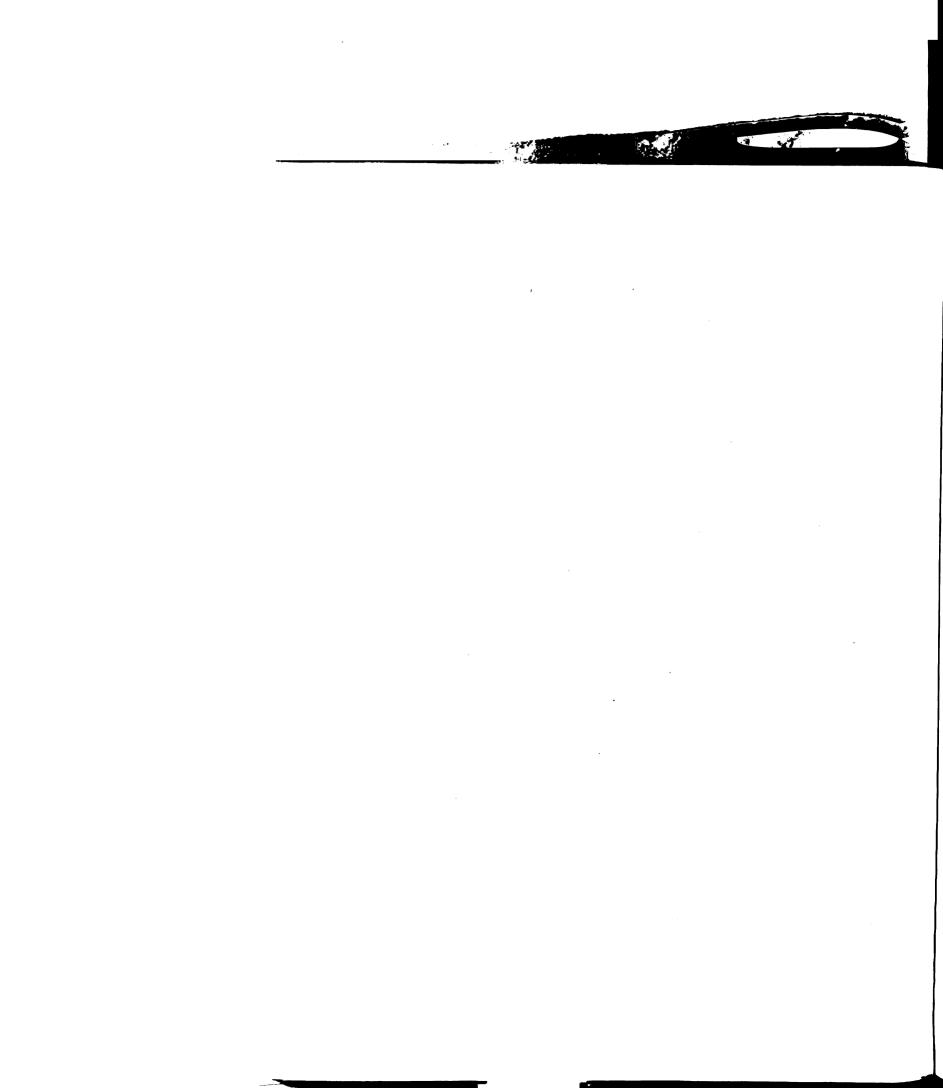


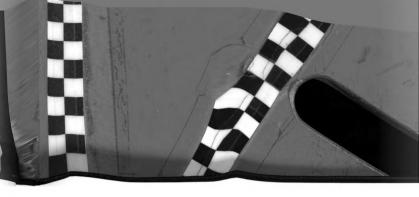


Modusker and Glams (38) found that the use of a boronic acid, rather than a boronic acid enhydride, as starting material for the preparation of alkyl diffuoroborones has the adventage of eliminating the dehydration step in the syntheses. The same paper reported a study of the reaction of halogenating agents with alkylboron oxides. The following halogenating agents were found not to react with the alkyl boron oxides: hydrogen chloride, thionyl chloride, phosphorus trichloride, silicon tetrachloride, and silicon tetrabroxide. Aluminus chloride reacted quite readily with the alkyl boron oxides in a manner similar to the boron halides, but with the production of a number of by-products. McCusker and Glums (38) suggested that the mechanism of the reaction involves as a first step, co-oxidinate bond formation between the oxygen of the alkylboron oxide and the boron or aluminum halide. The subsequent reaction mechanism could not be decided from the data however.

Physical and chemical properties of dihydroxy-n-butylborens  $(Q_0H_0B(0H)_2)$ , and its anhydride, 2,4,6-tri-n-butylborenine  $(Q_0H_0B(0)_2)$  have been reported in a study by Mattres, Brickson, and Lembengayer (39). Data are included on molecular weight in solution, vapor density, vapor pressure, density, refractive index, and for the latter only, viscosity, surface tension, and freezing point. The equilibrium between the dihydroxyborene, borine, and water is discussed by these authors.

Keller and Perrine (33) found tributylboracine to be vary stable in the absence of crygen and water, and to show no appreciable decomposition.





They found, however, that tributyl boroxine decomposed above 700° to yield predominabily triethylboroxine and ethylene. In the same study, these workers observed that tributylboroxine then treated with almainum chloride, phosphorus pentachloride, or boron trichloride yielded butyl-dichloroboxine, 3eBCl<sub>2</sub>, while the interaction of the compound with trimsthylalundnum, nethyl almainum iodide, or nethyl magnesium iodide yielded the analogous triallyl boxine, BuBNs<sub>2</sub>. Keller and Perrine (33) also found that triisobutylboroxine when treated with almainum chloride formed isobutume and boron trichloride instead of the expected isobutyl-dichloroboxine, iso-SuCl<sub>2</sub>.

t-Butylboron oxide was prepared by Johnson, Van Campen, and Grummitt (h0) by treating t-butylboric acid with thionyl chloride, who found it more advantageous to use the oxide then the acid in making solutions of a known quantity of the pure boronic soid.

Krause and Nobe (41) reported that tert-butyl boric acid loses water over phosphorus pentoxide in vacuum, but did not report chemical analysis nor a molecular weight for their product.

In a study on the stability, solvolysis, and co-ordination reactions of esters of boronic acids and their halogen derivatives, Brindley, Gerrard, and Lappert (h2) observed that traces of ferric chloride caused the decomposition of n-butylchlosboronite yielded n-butylchoric acids

R-BC1-OR - R-BO + RC1

Snyter, Eack, and Johnson (29) prepared n-hexylboron oxide by placing the crystalline n-hexylboronic sold in a dessicator over concentrated They found, housemy into equingly because dedeposes above 700° to plain predeminantly foligingly because and objection. In the same study, which predeminantly foligingly and objection of the folial production of the folial production of the state of th

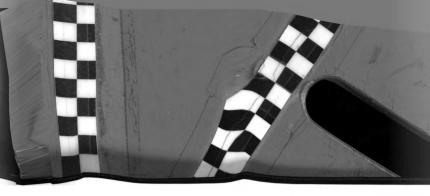
6-Sutylboron onlic non propored by (Gineen, Von Compan, and Genealth (10) by treating television and add things under the proposal to use the action than the critic to melting columbinar of the proposal to propose the proposal column.

Remay and Nobos (M.) repurbat that meri-jutyl barks deta tones, such as tones and the control of the control of

In a chaly on the standistry, solvelyade, and co-cathelder wascitons of setere of boronic soids and their indiages (arbivelyas, Sringley, Saranes, and Lapeach (12) changed that burches of fermin citocate caused the decempend of a burchistant of n-burgaletacheronates yielded n-burgaletacher as n-burgaletacheronates yielded n-burgaletacher as n-burgaletacheronates.

DH + 0545 = 30-054

Supter, Nack, and Johnson (29) proposed n-basylboren oxide by placing the aryskelline n-harylboresis next in a developer over conveniented



sulfuric acid or phosphorus pentoxide. The liquid anhydride, identified by boron analysis, was also prepared in the same study by refluxing the acid for one hour with an excess (3 moles) of thionyl chloride. On contact with water the oxide regenerated the boronic acid with slight evolution of heat.

19

References to a large number of anyl boroxines appear in the literature. The first such compound was prepared by Michaelis and Becker (h3) who reported that phenylboric acid upon distillation lost water to form phenylboric oxide,  $Q_{\rm e} H_0 B O_s$ 

The same workers found that if crystalline phenylboric acid is placed in a descionter for a long time, it is almost completely converted to phenylboric oxide. Krause and Ritsche (34) confirmed the work of Richaelis and Becker (43) by forming phenylboroxide,  $C_0H_0BO$ , by placing phenylboric acid over phesphorus pentoxide in a vacuum. Krause and Nobbe (14) observed that phenylboric oxide and magnesium ethyl broadle reacted vigorously, and that the product when distilled gave boron tricthyl,  $B(C_0H_0)_3$  and boron triphenyl,  $B(C_0H_0)_3$ . The molecular weight studies of Kinney and Ponta (25) on phenyl boron oxide have already been mentioned.

Brindley, Gerrard, and Lappert (h2) prepared esters of phonylboronic acid by esterification of phonylboronic anhydride with the appropriation alcohol by an assotrope method.

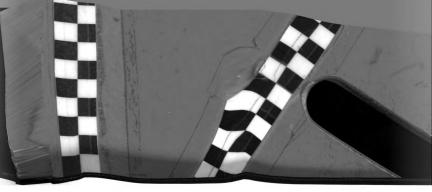
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Able, Dandeganker, Gerrard and Lappert (hh) interacted boron trichloride with phenylboronic ambudride in an inert solvent at -80° to prepare phenyldichlorborane, PhBCl<sub>2</sub>.

Michaelis and Behrans (h5) dehydrated e-tolyhboric acid, c-naphthyl boric acid, and f-naphthyl boric acid in a descicator over sulfuric acid, and identified the resulting oxides by boron analyses. Michaelis (h6) also obtained the anhydrides of 2,h-(Gi<sub>3</sub>)<sub>2</sub>C<sub>H3</sub>B(Gi)<sub>2</sub>, 3,h-(Gi<sub>3</sub>)<sub>2</sub>C<sub>H3</sub>B(Gi)<sub>2</sub> and 2,5-(Gi<sub>3</sub>)<sub>2</sub>C<sub>H3</sub>B(Gi)<sub>2</sub>. Since Knivila and Hendrickson (h7), in a study on the rates of brominolysis of substituted benseneboronic acids, found that benseneboronic acid and its subydride yielded the same specific rate constants, they felt justified in using the acid in some cases (p-BrC<sub>H4</sub>- and m-C<sub>2</sub>H<sub>2</sub>OOCC<sub>H4</sub>-) and the anhydride in the following cases:

p-GH<sub>3</sub>OC<sub>3</sub>H<sub>4</sub>m-NO<sub>2</sub>C<sub>3</sub>H<sub>4</sub>p-C1C<sub>3</sub>H<sub>4</sub>p-G1<sub>3</sub>C<sub>3</sub>H<sub>4</sub>m-G1<sub>3</sub>C<sub>3</sub>H<sub>4</sub>m-G1<sub>3</sub>C<sub>3</sub>H<sub>4</sub>p-C<sub>2</sub>H<sub>3</sub>OC<sub>3</sub>C<sub>4</sub>H<sub>4</sub>-

Been and Johnson (18), while studying the action of derivatives of phenylboric acid upon bacteria, reported that p-bromophenylboric acid melted with decomposition at 286-289°, resolidified, and remelted without resolidification at 301-302°; they assumed the latter to be the melting point of the anhydride. The same anhydride, p-bromophenyl-, was reported by Konig and Scharmbeck (19) along with the m-emisyl-, p-tolyl-, and G-maphyl- derivatives.

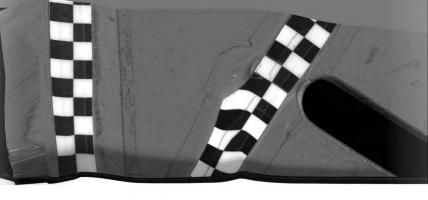
Brench, Esbroff, and Bettmen (50) reported that if o-chlorophenylboric sold is heated below its multing point (m.p. = 97-98°) the anhydride Ablas Dandograians, Oceanic and Lappare (Mg) inhuranted boron telchloride whin planyiperanic subjection in allers solved at -80° to proper planyiditalizations, which;

idinoslin and Deirena (AS) issignized o-colylicate over sulfuria soil, being beath and p-aspiring being soil in a descirate over sulfuria soil, and fearthfied the resultance origin by beron analysms. Mehestis (ES) and identified the resultance of 2,1-(Ug),20458(M), 3,1-(Ug),20468(M), 3,1-(Ug),20468(M), and 2,1-(Ug),20468(M), and 2,1-(Ug),2046(M), and a conjugation of midualishmin beatsunbounded with the return of beatsunbounded and an expectation of midualishmin beatsunbounded and an epocific return complexed to units the sense of the sense (p-3004), and the units and the sense of the consection of the confusion of the consection of t

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Bearin, Sabrett, and Sabbann (50) separated that Mr o-collected substantial bearts at the sound the substant policie (n. o. o. 74-50) the enture of the collected substantial substantial



slowly forms and the sample does not mult until 167-168°. Some of the acid was dehydrated in a vacuum descinator containing concentrated sulfuric acid; the amhydride thus obtained (loss of water correct for the Ar80 compound) melted at 171-172°. In the same paper, mention is made that m-phenetylboric acid and p-phenetylboric acid mult rapidly with the liberation of moisture and resolidify to form new solids (anhydrides) which mult approximately 20° above the respective acid. No chemical analysis or molecular determinations were made on any of these reported anhydrides.

In a study of the relative strengths of some hydrocarbon derivatives of boric acid, Ishroff, Branch, and Bottman (51) reported that o-diphenylboric acid forms long needles which mult at 129° with affervescence; after multing resolidification takes place; the new solid (the anhydride) multed at 195°. In the same study, a sample of benzylboric acid upon drying, became warm, gave off white fumes, partially multed, and shrank to an amorphous mass which consisted almost entirely of boric acid.

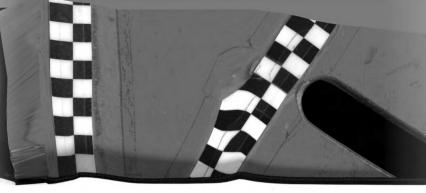
Although other samples did not behave in this manner, Lappert (h), in his review, lists this reference as a preparation of benzylboroxins.

While studying the dissociation constants of organic boric acids, Bettaen, Branch, and Rabroff (52) found that o-mitrophenylboric acid malts at 101° (instant immersion) and resolidifies to malt at 115-117°. This malting point corresponds to the value of 113.5-117.7° observed by Season and Johnson (53) for the substance obtained by drying o-mitrophenylboric acid in a vacuum dessicator over sulfuric acid. The latter workers

singly form and the scape does not until 157-150°. Some of the
antitate entity the anyoride time obtained (loss of seven contentes)
the ACO acapaint) matted at 177-170°. In the same paper, marking in
the ACO acapaint) matted at 177-170°. In the same paper, marking in
acts that membershive at 177-170°. In the same paper, marking in
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To chemical analysis or rejection according the time respective sold.
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In a study of the relative strengths of some hydrocarbon derintries of bords and, Tehredt, Burnett, and Buthens (31) apported that ordering bords sold from long modiles which make at 129° with afterwaresones after modified resolutified at 195°. In the same white, a sample of beautyloude and there and the first distribution of the same and th

Beliaus, livence, ent Introd. (\$2) faint that c-disconinglement hold redite at 101° (instant insuration) and resultaining to make the life of life faint point coveragence to the value of 115.5-117.7° deserted by Semen and Johnson (\$3) for the schools of site in the destroy of the life in the coverage of the life in the latter emission beets seld in a vacuum descinator over militario ands. The latter emission



confirmed the formula for the anhydride,  $NO_nC_0i_13=0$ , by nitrogen analysis. Seeman and Johnson (53) also found that m-nitrophenylboric acid formed the anhydride when dried to constant weight in a dessicator in vacuo over concentrated sulfuric acid. In the same study, Seeman and Johnson dried m-aminophenylboric acid to constant weight in a vacuum dessicator (10 days) over sulfuric acid. Kjeldahl analysis yielded results of 11.11 and 11.12% nitrogen. These results were compared with the calculated percentage nitrogen for:

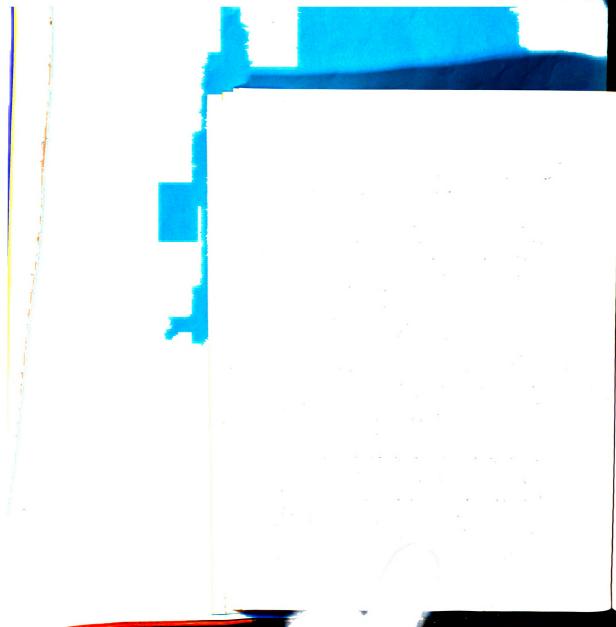
MigC\_H\_B(OH), 10.23

ME\_C\_H\_BO 11.78

(NH -C -H\_BOH) -0 10.95

The nitrogen determinations indicated to the investigators that the completely dried sample was an analydride formed by the elimination of one molecule of water from two molecules of the acid. An explanation by Seaman and Johnson of the formation of this type of enhydride is that the aminoacid may exist as a salt (as do glycine and sulfamilie acid) formed by intramplecular neutralization; thus the elimination of a molecule of water can only occur between two molecules:

Another class of compounds of the type (BOX)<sub>3</sub> is the haloboroxines, in which the X is a halogen. Probably the first indication of such compounds was in studies by Wiberg (5h) and co-workers on the reaction of boron trichloride with alsohols and others in which dichloroboric





stid esters,  $BGl_0/R$ , were found. There was formed in the thermal decomposition of the dichloroboric acid ester a solid white substance for which the authors assumed the formula BoCl and which was extensively decomposed into  $B_0O_0$  and  $BGl_0$ .

Banagarten and Bruns (55) proposed a heterocyclic six-ring structure for the reaction product of boron trickide and boron trifluoride and considered it as a tripolymer of BOF, and not an addition product. The same paper proposed the unstable boron cayfluoride (BOF)<sub>3</sub> for the reaction product of some alkali and alkaline earth salts with boron trifluoride at 150°. Equations for some of the reactions of Banagarten and Bruns are given as follows:

$$3 \text{KBO}_2 + 6 \text{BF}_3 \longrightarrow 3 \text{KBF}_4 + 2 (\text{BOF})_3$$
 $6 \text{KNO}_2 + 9 \text{BF}_3 \longrightarrow 6 \text{KBF}_4 + (\text{BOF})_3 + 3 \text{N}_3 \text{O}_3 (2 \text{NO}_2 + \text{K}_3 \text{O}_2)$ 
 $3 \text{K}_3 \text{CO}_3 + 9 \text{BF}_3 \longrightarrow 6 \text{KBF}_4 + (\text{BOF})_3 + 3 \text{CO}_3$ 
 $3 \text{Ce}_4 \text{(Ng)} \text{CO}_3 + 3 \text{BF}_3 \longrightarrow 3 \text{Ce}_4 \text{(Ng)} \text{F}_2 + (\text{BOF})_3 + 3 \text{CO}_3$ 

In later work Baumgarten and Brune (56) studied the reactions of boron trifluoride with aluminum oxide, silicon dioxide, titemium oxide and silicates. The reaction with aluminum oxide occurred at about  $1,50^{\circ}$  according to the reaction

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Designation and Numan (55) proposed a heterodyplic also-sing stands and for the reaction product of borns tringide and haten tringide and considered it as a tripingular of DOS, and not an addition product. The case paper proposed the untained bares conflictated (NOF), for the resention product of one almost an adjustice and a sufference at the paper to see that the paper to see the conflictation of the resentions as follows:

In later west surjected and large (56) ebuiled the transition of boost trillection with electron and allocates. The remarks also algorithm and allocates. The remarks also algorithm and allocates to shoot has a sent to according to the restation

and willised, presumably as the oxyfluoride. Other typical reactions in this study were:

$$3$10_{3} + 60F_{3} \longrightarrow 3$1F_{4} + 2(00F)_{3}$$
 $1510_{3} + 30F_{3} \longrightarrow 10F_{3} + 81F_{4} + (00F)_{3}$ 
 $3(Al_{2}O_{3}-2510_{3}) + 210F_{3} \longrightarrow 6AlF_{3} + 651F_{4} + 7(30F)_{3}$ 

pared by Goubeau and Keller (16) from boron trioxide and the respective boron trihalide at temperatures above 250° under normal pressure. These investigators found the volatile, gaseous haloboroxoles to decompose, on cooling, back to boron trioxide and boron trihalide by way of non-isolated intermediate steps. In the same study, measurement of the temperature coefficient of pressure showed that these compounds correspond to the trimeric formulae between 250 and \$10°. Another paper by Goubeau and Kaller (57) gives an extensive study to prove the trimeric nature of trichloroboroxole. Goubeau and Keller (17) have also presented the Raman spectra of trichloroboroxole in support of a six-membered B<sub>3</sub>O<sub>3</sub> ring.

Tri-dimethylaminoboroxole, B<sub>3</sub>O<sub>3</sub> k(2i<sub>3</sub>)<sub>2</sub>]<sub>3</sub>mes formed by Coubeau and Keller (16) from boron trioxide and tri(dimethylamino)borine at 260-300° and 10-15 atmospheres in 3-k hours. The well-orystallised compounds hydrolysed easily with water to form borin acid and dimethylamine. The trimeric formula was determined by vapor pressure measurements and also by ebullioscopic measurements in became.

and the thin becomenter the burst belogies reposed with boxes trichland and voletilities, presently as the originaries. Other typical emergians in this blady name:

$$3010_0 + 637_0 - - 3034_0 + 2(307)_0$$
 $3010_0 + 337_0 - 307_0 + 617_0 + (507_0)_0$ 
 $3(10_0 + 617_0 + 617_0 + (507_0)_0)$ 

Indiandemonole, entriburescondia, and triburesconderent prove propresed by Serbene and Sellar (16) lyes before triburesconding and the composition
before builded at traperatures some 200 mater means produced. This
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Tel-directive incomments, hote M(0), alone toward by income and realize (16) from toward to the continue of the first telescope and the continue of the contin



Metaborenilide, Gelekillo, was prepared by Chandhuri (58) by heating a mixture of boric soid, smiline, and fused sine chloride at 135-140°.

In Lappert's review (h) mention is made that "no physical measurements were made, but it seems possible that metaboranilide is trimeric and hence a boraxole." Chandhuri, however, gives data for monomeric CoHoNEBO, as determined by the platinicileride authod.

A repid increase in interest of the boronines for industrial use is evident from recent chemical news items and technical data sheets.

Trinsthosphoronine is now a commercial production item of Anderson Chemical Company. Originally requested to make the compound for use in evaluation of the action of boron compounds on engines using high energy fuels, Anderson (59) says its product is now being used in testing special engines, as a paint formulation ingredient, and as a fire extinguisher fluid.

Anderson anticipates that trinsthosphoronine may be used in many applications, such as an automotive fuel additive, a test additive for jet fuels, a formulation of self extinguisher fluids, a treatment of fibrous materials for fire resistance, a formulation of heat resistant plastics, a formulation of quick drying printing inks, a dehydrating agent in chemical reactions, and a neutron detector. It is also significant to note that methyl, isopropyl, and n-butyl metaborate esters are available connercially.

Commercard, Chamberlain, and Shephard (60) found trimethougheresine to be a liquid having unique characteristics which were useful for Arthogogalita, Odukuo, men papunan by Guanduri (58) by Ascidor
A steiners of books sett, salitas, sat Nami she chlocks st 155-150°.

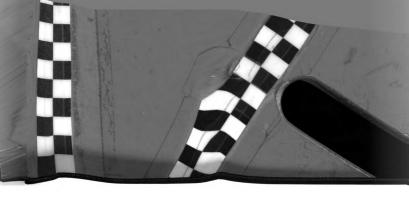
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In layurch's review (b) section is ando that 'no physical securements were seen, but it evans possible that artsbourgalishe is trimpade and bease a bourchist.

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extinguishing fires due to such metals as magnesium, titenium, and sireonium. Small sodium and sodium-potassium alloy fires were also controlled by the agent. 26

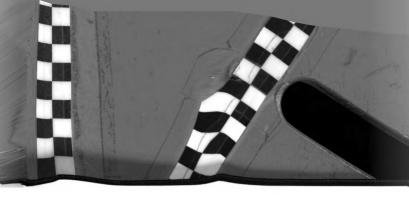
Further mention of the future of boroxines is made in an article

(61) on "What's New for Boron?" In this general interest article,
American Potach and Chamical state their optimism that the boroxines
will find widespread applications in industrial processes in which high
boron content compounds in liquid form are desired.

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#### I. PREPARATION AND PROPERTIES OF SOME ALKOXYBOROXIMES

### Introduction

The first boroxines formed were trimethony- and triethoxyboroxine, prepared by Schiff (13) by dissolving boron trioxide or orthoboric acid in the trimethyl and triethyl esters of orthoboric acid, respectively.

Goubean and Keller (16) used a modification of the procedure of Schiff to prepare trimethoxyboroxole, and corried out the first study of the properties of the compound. Ogle (7) prepared and investigated some physical properties of trimethoxy- and tri-n-butoxyboroxine. A recent study of the preparetion, properties, and structure of trimethoxyboroxine was made by Carpenter, Rughes, and Bergman (18). Since the completion of the experimental work of this thesis study, Leppert (25) has published an article on the preparation of methyl-, ethyl-, n-propyl-, isopropyl-, n-butyl-, isobutyl-, and sec-butyl metaborate.

At the start of this thesis project, however, the only alkocyboroxines previously studied were the trinsthoxy- and tri-n-butoxy- compounds.

Thus an investigation was undertaken to prepare and study some higher homologues of trimsthoxyboroxine.

In this dissertation study, the method of Goubean and Kaller (16) was used to prepare triethour, tri-n-propage, tri-n-butage, triiso-butage, tri-sec-butage, tri-n-pantage, tri-n-octage, and tri-n-do-decoxyborazine. The preparation of tricthoxyborazine is given in detail

C. PREPARATION AND PROPERTIES OF SCHA ALECTROPOLITIES.

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In the tribution or estimated corresponds or estimated acts of the tribution of the property of the distortion of the property of the distortion of the property of the follows the follows the first property of the properties to the compound of the first and strength of the string of the properties of the compound the first-probagoons as the properties of the entire at the properties of the entire the first properties of the entire the first properties of the properties of the entire that the properties of the theory and the entire that the properties of the theory of the properties of the theory of the theory of the properties of the theory of the properties of the third the theory of the properties of the third the theory of the properties of the third the theory of the properties of the theory of the theory of the properties of the theory of the theory of the properties of the theory of the properties of the theory of the theory of the properties of the theory of the theory of the theory of the properties of the theory of the the theory of the theory of

At the start of this limit project, source; the only alleadynamics
proviously chained were the telephony—and tris-a-baimp- captains.
Thus at investigation was underwise to project and shall note higher bankings of telephony-arasing.

The first extransional mindy, the notices of drabest and lighterthe soul to propose traditions, and-o-proposes, and-o-tradegs, traditionintegral and excellency, and-o-proposes, and tradeg-odescriber of the proposetion of original proposes is given in detect in the Experimental of this Sections the preparation of the other boroxines is summarized. The boiling point and freezing point of each compound was observed, as recorded in Table 2. The density of each compound was observed over a range of temperatures. The boroxines were found to be soluble in a number of organic solvents such as borsone, toluene, distingly ether, carbon tetracialoride, and chloroform. Molecular weights, determined abullioscopically or organically in benzone, showed the compounds to be trimeric. The boroxines hydrolysed in water to form, presumably, orthoboric acid, and the corresponding alcohol. The addition of other solutions of a number of aromatic anines to other solutions of trimethoxy— and triothoxyboroxine yielded precipitates; no visible precipitates were observed when the other boroxines were used.

# Benerimental

# Triethambaradae

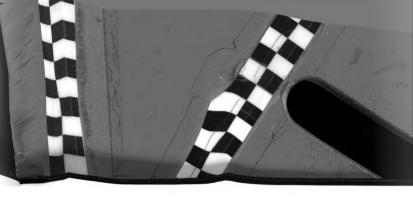
To prepare tristhomyboroxine, the two reactants, diboron trioxide (50.0 g., 0.840 moles) and tristhomyborene (122.5 g., 0.840 moles) were heated under reflux in a round-bottom flack at a temperature such that the tristhomyborene would drip slowly back into the flack. The mixture was stirred repidly by a glass-covered magnetic stirring bar. The top of the reflux condensor was fitted with a drying tube filled with Drierite. After six hours of heating the diboron trioxide appeared to be completely dissolved. The viscous liquid was allowed to cool to room temperature and was then filtered through sintered glass into a glass stoppered flack. The flack was stoppered and placed in a -73° C. bath

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The property translater pharmeter, who has restante, absorber (122.5 a., 0.600, index) mass (150.0 a., 0.600, and a passe (150.0 a., 0.600, and a passe (150.0 a., 0.600, and a passe that the state of a passe plane that the destruction of a passe plane. The alcohology between a substanted republic to a plane-arrow angular and a translate to a passe plane. The translate of the angular and a passe and a passe of the alcohology and a passe of the angular and a passe of the angular angular and a passe of the angular a



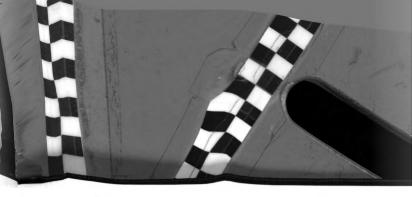
of dry ice and isopropyl alcohol for six hours; the liquid free solid. The flask and its contents were allowed to heat up to room temperature, whereupon the frozen compound melted and the product was stored in a place-stoppered bottle.

29

The colorless, viscous compound hydrolysed rapidly in water. (In some of the runs the preparations were light-yellow liquids.) The compound was analysed for boron by dissolving and hydrolysing it in hot water and titrating the liberated boric soid with standard base, using mannitel, according to the procedure cutlined in Kolthoff and Sandell (62). The compound was found to contain 15.3 per cent boron (theoretical percentage for  $(C_2E_3OBO)_3$ , 15.2). The molecular weight, determined cryoscopically in bemsens was found to be 210 (theoretical for  $(C_2E_3OBO)_3$ , 215).

The triethoxyboracine from as a clear glass at approximately -1.5° C. A flask containing a thermometer wall was used in the determination of the boiling point so that both the liquid and vapor temperatures could be observed when the distillate was collected. No distillate appeared until the flask thermometer resched 21.0° C. At this time the thermometer registering the vapor temperature rose rapidly (from approximately room temperature) to 107° C., and liquid appeared in the condensor. The majority of the liquid distilled at 107-109° C., leaving in the flask a gumy residue of boron trickide. Analysis of the water-clear distillate showed 7.50 per cent boron (theoretical percentage for (C<sub>2</sub>H<sub>2</sub>O<sub>3</sub>)<sub>3</sub> B, 7.41.

The density of the tristhoxyboroxine, from  $0.0^\circ$  C. to  $80.0^\circ$  C. was determined by using a one-millilitor dilatometer. The dilatometer was



weighed empty and then filled with tristhoxyboroxine and reweighed.
The volume was obtained by reading the liquid level on the graduated stem to within 0.001 cc. The dilatometer was immersed in a Desar flack until the liquid level in the dilatometer was covered with water of the desired temperature. The temperature was measured, using a National Bureau of Standards thermometer, accurate to within ± 0.1° C. The data for the density determinations of triethoxyboroxine are given in Table 5. The following equation giving the density of the triethoxyboroxine from 0.0° C. to 80.0° C. was calculated from the experimental density data

where t equals degrees centigrade.

The triethoxyboroxine is miscible with bemsens, toluens, ethyl ether, acetone, carbon tetrachloride, and chloroform. Two milliliters each of triethoxyboroxine and the respective solvent were used in the mixtures.

Since reactions of various kinds of boron compounds with ammonia and its derivatives have been of interest, ether solutions of a number of aromatic amines were added to other solutions of triathoxyboroxine.

Solid compounds to which the following empirical structure has been assigned were obtained:

The nature of this reaction is discussed in more detail in Section II, page 46.

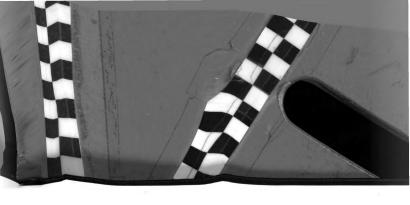
# Tri-n-propogy tri-n-butogy tri-sec-butogy triiscbutogy, tri-n-butogy tri-n-dodecom boroxing

The preparation of these alkoxyboroxines followed the procedure detailed for tristhoxyboroxine and will only be outlined in this next section. A peddle stirrer was found to be more efficient than a magnetic stirrer. The diboron trioxide appeared to dissolve more readily in the higher molecular weight alkoxyboranes, probably due to the higher boiling points of these compounds.

The tri-m-dedecoxyboroxine was a white war-like solid at room temperature; the other boroxines studied were viscous compounds at room temperature. The tri-m-propoxy-, tri-m-butoxy-, tri-sec-butoxy-, and tri-isobutoxyboroxines were water-clear liquids (although some preparations of the tri-m-propoxyboroxines yielded a light yellow liquid). The tri-m-pentoxy- and tri-m-octoxyboroxines were clear light yellow liquids.

Prolonged heating of the yellow compounds tended to cause them to darken.

Upon distillation each of the boroxines decomposed to split out a water clear distillate and leave a gusny residue high in boron content. The distillates were analyzed for per cent boron; the results of the analyses (Table 2) indicate that the distillates were the corresponding trialkoxy-borenes. The temperature at which each boroxine decomposed and also the temperature at which the corresponding distillate condensed are given in Table 2. In all cases the decomposition temperatures (that of the liquid in the flask) are higher than the vapor temperatures (at which the



vapor condensed). The temperatures at which the boroxines became solids are given in Table 2. The tri-n-propoxy-, tri-n-butoxy-, tri-isobutoxy-, and tri-n-pentoxyboroxines froze as clear glasses; the tri-esc-butoxyboroxine became a white solid. In an attempt to obtain the freezing point of tri-n-octoxyboroxine, the solution remained a clear-yellow until -25°C. At this point, the compound became a white solid. Upon warming the compound appeared to melt slightly shows -25°C., but remained a white liquid until the temperature was 5°C., at which time the color changed to yellow again. The same results were obtained with and without a jacketed freezing point tube.

The boroxines hydrolysed in water; the rate of hydrolysis appeared to diminish with increased molecular weight of the compounds, being especially slower for the tri-m-octory—and tri-m-dodeoxyboroxines.

The formation of an insiscible substance (probably m-dodeoxyboroxines) was apparent in the hydrolysis of tri-m-dodeoxyboroxine.

The boroxines were analysed for boron by dissolving and hydrolysing them in hot water and titrating the liberated boric acid with standard base, using mannitol, according to the procedure cutlined in Kolthoff and Sandell (62). To assure complete hydrolysis in the analyses of the tri-n-cotony—and tri-n-dedecompoundmes, these compounds were dissolved in hot water in icdine flasks, the flasks stoppered, and the solutions kept hot for two and four hours, respectively. The solutions were cooled to room temperature before titration. The results of the boron analyses are given in Table h; in all cases the percentage of boron

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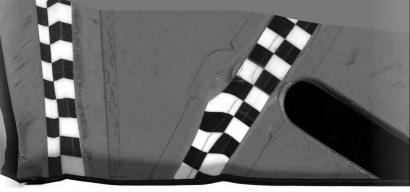


Table 2
MELTING POINTS AND DECONTOSITION POINTS OF THE BOROXINES
AND BOILING POINTS OF THE DISTILLATES

R in (ROBO) <sub>3</sub>	Melting Point of (ROBO) a	Decomposition Point of (ROBO)3	Boiling Point of Distillate C.
Methyl	10 <sup>8</sup>	170ª	68 <sup>a</sup>
Ethyl	-45	210	107-109
n-Propyl	-28	265	177
n-Butyl	-63	295	240
iso-Butyl	-10	276	207
sec-Butyl	-13	258	184-186
n-Anyl	-50	340	240
n-Octyl	-25	275/2 mm.	190/2 ma.
n-Dodecyl	30	310/2 mm	275/2 mm.

aReference 16.

bNo distillate at 375° at 1 atm.

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Deplays	305	1700	68 <sup>6</sup>
20gg.	-145	210	Sort-Aort
Logori-a	89-	265	LAT
Delation	0-	295	O.IS
Lorun-oul	0.0-	276	PUS
eso-Dulpi.	CL-	858	381-386
Ligat-m	-50	DEE	240
In-Outpl	-25	200 S/293	190/2 m.
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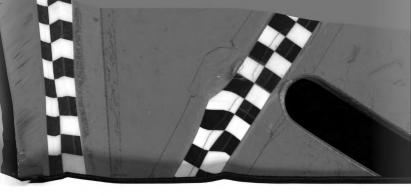


TABLE 3
BORON ANALYSES OF THE DISTILLATES FROM THE BOROXINES

R in (ROBO)a	Per Cent B Found in Distillate	Per Cent B Calculated for (RO) <sub>3</sub> B
Ethyl	7.50	7.41
n-Propyl	5.83	5.75
n-Butyl	4.60	4.70
iso-Butyl	4.72	4.70
sec-Butyl	4.80	4.70
n-Anyl	4.05	3.98
n-Octyl	2.65	2.71
n-Dodecyl	2.02	1.91

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20,000	78.5	74.5
THIS THE	5.83	
Definition	4.60	04-1
Derug-out	Sy. a	04-1
Ly31/5+000	08.4	09.4
n-Aug 2		3.98
2-00tg/1	30.5	14.2
Dypolodier	2,02	1.91

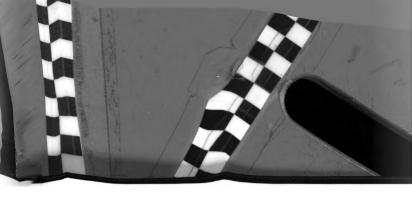


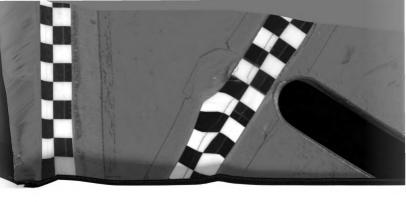
table 1.

Boron analyses and polecular valuets of the boroxines

		Cent B	Molecu	ler Weight
R in (ROBO) <sub>3</sub>	Found	Calculated	Found	Calculated
Ethy1	15.3	15.2	210	215
n-Propyl	12.6	12.7	261	257
n-Butyl	10.8	10.9	290	299
iso-Butyl	11.0	10.9	292	299
sec-Butyl	10.8	10.9	305	299
n-Amyl	9.69	9.58	330	341
n-Octyl	6.91	7.00	1480	467
n-Dedecyl	4.92	5.00	604	625

DESCRIPTION AND AND PARTIES FOR MALDING ON THE DESCRIPTION

	calcinia de la constanta	noa Felli bruso T	E 3msQ begalands	Total Post	a(comp) mit m
h	12.5	210	15.2	25.3	Provide
	257	261	3,2.7	3.8.6	ing spings.
	283	290	30.9	20.8	Provide a
	299	292	20.01	33.0	Intel-out
	299	305	20.01	10.8	September 1
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	1,67	084	7.00	5,93.	April 16- Control
	625	al0è	5.00	\$8.3	Application /
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found agreed with the value calculated for the trialkonyboroxine, (ROBO)3.

The nolecular weights of the boroxines were obtained either shalloscopically or cryoscopically in beasons. The results obtained (Table 4) indicate that the compounds have the trinsmic formula, (ESBO),.

The densities of the boroxines, from 0.0-30.0° C., were determined by the same dilatoxeter method as with the tristhoxyboroxine. The density data are given in Tables 6-10. From the density data obtained for each boroxine, an equation

#### D = a + bt (t equals degrees Centigrade)

was calculated for that boroxine. These equations, and the density of each boroxine at 25° C. calculated from the equation, are given in Table 11.

The boroxines are miscible with bensens, toluene, ethyl ether, acetone, earbon tetrachloride, and chloroform. Two milliliters each of the boroxine and the respective solvent were used in the mixtures. Solution was not as repid with tri-m-dodeoxyboroxine as with the other boroxines, and was aided immensely by stirring.

No attempt was made by this worker to recover the boroxines from the solvent, but Lappert (25) recovered the boroxines from such anhydrous, volatile solvents as asthylene, dichloride and sthyl other by evaporation of the solvent.

Unlike the trimethoxy- and triethoxyboroxines, the addition of other solutions of smiline and ring-substituted amilines to other

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The election relative of the benediate were desired either equilibries and contents or enveloped (finite it) benediate that the employed into the translate (exactly, each the employed into the translate (eachly,

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use edicaters for that borneths. These equations, and she density of and reference at 25° C. enterlated from the equation, and given in Twite II.

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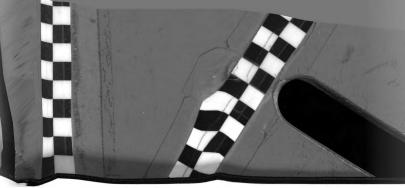


TABLE 5
DESSITY OF TRININGSOROXINE

Temperature (°C. ± 0.1)	(g./e.c., ± 0.001)	Calculated Density (g./e.c., ± 0.001)
0.0	1.113	1.113
10.0	1.102	1.102
20.0	1.091	1.091
30.0	1.080	1.080
40.0	1.070	1.069
50.0	1.059	1.058
60.0	1.048	1.047
70.0	1.038	1.036
80.0	1.028	1.025

<sup>\*</sup>D = 1.113 - 0.0011 t

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Calculated Danel (g./d.o., 2 0.00	Township Tenedicy (6-/0-0-, 1; 0-001)	("C. 2 0.1)
 1,113	1.13	0.6
1,102	90£.£	10.0
100-1	2,092	SUOD STATE
3,4080	1.080	goug
1.089	2.070	0.63
1,038	2,899	2010
2,000	340.1	0.03
1.736	2,433	0.09
500.1	1,028	0.05

" = 3.113 - 0.002 b

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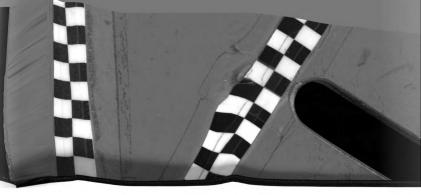


TABLE 6
DENSITY OF TRI-n-PROPOXYBOROXINE

Temperature (°C. ± 0.1)	(g./c.c., ± 0.001)	(g./c.c., ± 0.001)
0.0	1.047	1.047
10.0	1.038	1.037
20.0	1.027	1.027
30.0	1.017	1.017
40.0	1.008	1.007
50.0	0.998	0.997
60.0	0.988	0.987
70.0	0.978	0.977

<sup>\*</sup>D = 1.047 - 0.0010 t

SECRETARIOS SOCIEDAS SOCIEDAS

Calminated Density (2 (2 / 4 vo. 2 )	(200.0 ft (10.00.2)	(£.0 ± .0°)
Dio-T	1.4867	0.0
1.037	860.1	0.02
1.027	1.027	3040
7.03.7	1.017	avog
1,000	600.I	0.04
166.0	824.0	50.0
789.0	889.0	0.03
116.0	879.0	70.0

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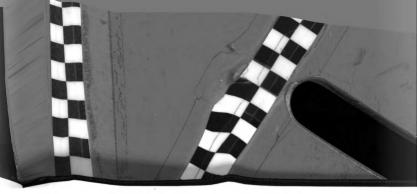


TABLE 7
DENSITY OF TRI-Sec-BUTOXYBOHOXIDE

Temperature (°C., ± 0.1)	Observed Density (g./c.c., ± 0.001)	Calculated Density (g./c.c., ± 0.001)
0,0	1.091	1.090
10.0	1.061	1.081
20.0	1.072	1.072
30.0	1.063	1.063
40.0	1.054	1.054
50.0	1.045	1.045
60.0	1.037	1.036
70.0	1.028	1.027
80.0	1.019	1.019

<sup>&</sup>quot;D = 1.090 - 0.0009 t

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A STREET

(BOLD to county)	19224790 (201508100 (200,0 ± 10,00%)	(丘原金山門)
080.1	2,9,4	0,0
1.001	19061	3040
1,072	SEDAL	0,09
glo.z	5004	20.0
20.0	1.085	0,40,6
7.06	1,065	0.05
34036	14037	0.48
14002	1,088	0.00
71000	7.019	0.08

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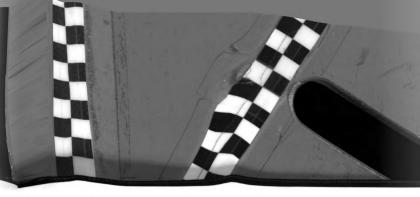


TABLE 8
DENSITY OF TRIESCRUTOXYBOROXINE

Temperature (°C., ± 0.1)	Observed Density (g./c.c., ± 0.001)	Calculated Density (g./c.c., ± 0.001)
0.0	1.098	1.098
10.0	1.088	1.088
20.0	1.077	1.078
30.0	1.067	1.068
40.0	1.058	1.058
50.0	1.048	1.048
60.0	1.039	1.038
70.0	1.030	1.028
80.0	1.020	1.018

<sup>\*</sup>D = 1.098 - 0.0010 t

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Caloning maintening (E/0.10.1 ± 0.001)	Character Donalty Levens 2 0000)	Tendestara (V., 2 0.1)
2.00	Section	0,0
1.068	1,088	0.01
2,098	TWEE	0.08
2,088	1.087	0.06
1.033	1,050	0,0
1.008	BAOL I	50.0
2.038	950.1	0.08
Hau. I	1,090	0.05
1.038	1.30	0.08

# 0500.0 - BQO.E - 0



TABLE 9
DENSITY OF TRI-12-PENTOXYBOROXINE

Temperature (°C., ± O.1)	(g./c.c., ± 0.001)	(g./c.c., ± 0.001)
0.0	1.095	1.096
10.0	1.065	1.085
20.0	1.076	1.076
30.0	1.067	1.067
40.0	1.058	1.058
50.0	1.00	1.049
60.0	1.040	1.040
70.0	1.031	1.031
80.0	1.023	1.022

<sup>\*</sup>D = 1.096 - 0.0009 t

CALLEY OF THE CHINAMETER OF THE CONTRACT

Outgoing the footing (Colors of the Colors)	(Billion torrest)	The succession (Co., suc.)
1.096	3,4095	0.0
1.058	1.055	20.0
940*1	240-1	0.08
1.067	3.089	0.00
1.028	37,058	0.04
1,019	Mo.I	50.0
1,050	nan.s	0.69
1,032	15041	0.08
1,022	CAL	0.08

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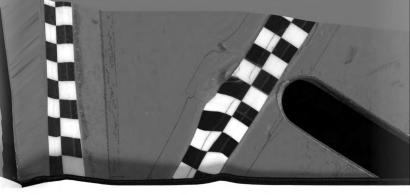


TABLE 10
DESCRIPT OF TRI-M-OCTOXYBOROXINE

Temperature (°C., ± 0.1)	Observed Density (g./e.c., ± 0.001)	Calculated Density (g./c.c., ± 0.001)
0.0	0.937	0.936
10.0	0.930	0.929
20.0	0.922	0.922
30.0	0.915	0.915
40.0	0.908	0.908
50.0	0.901	0.901
60.0	0.894	0.894
70.0	0.887	0.887
80.0	0.881	0.880

<sup>\*</sup>D = 0.936 - 0.0007 t

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(EULO 2 .o.o\z)	(geless) femily (geless) 10.00	Tapparokers (*0.± c.l)
0.936	750.0	0,0
0.929	059.0	2010
500.0	250.0	0.08
516.0	326.0	30.0
80%,0	899,0	0.08
DOD, O	0.900.	0.08
16000	458-0	0.00
788.0	788.0	0.05
0,880	160.0	0.08

# 7000.0 - 888.0 = a

TABLE 11
EQUATIONS FOR DENSITIES AND CALCULATED DENSITIES AT 25°C.

R in (ROBO)3	Equation for Density	Density at 25°C. (calculated)
Nethyl	D = 1.242 - 0.0012 ta	1.212
Ethyl.	D = 1.133 - 0.0011 t	1.136
n-Propyl	D = 1.047 - 0.0010 t	1.022
n-Butyl	D = 1.030 = 0.009 ta	1.006
iso-Butyl	D = 1.098 = 0.0010 t	1.073
sec-Butyl	D = 1.090 = 0.0009 t	1.078
n-Anyl	D = 1.096 - 0.0009 t	1.074
n-Octyl	D = 0.936 = 0.0067 t	0.919

E Reference 7.

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Bytoes.	By \$200,0 - \$43.1 = 0	1,212
£950	D = 1.133 - 0.0011 6	1.136
Individual.	p = 1.007 - 0.0020 t	2.022
Dyfall-a	D = 1.030 - 0.009 20	1.008
Detail-out	\$ 0,000.0 - 800.1 - G	Elo'T.
Defect-one	D = 1.090 - 0.0009 t	3,076
dyst-st	9 600000 - 96011 - 0	1.0%
Eqfeli-a	5 4900°0 - 966°0 = G	eten

"Jacomence 7.



14.

solutions of the higher boroximes did not yield any visible precipitates. (These reactions are discussed in detail in Section III, page 46.)

## Discussion

The method of Goubean and Keller (16) was used to prepare triethony. tri-n-propony-, tri-n-butony-, trisobutony-, tri-sec-butony-, tri-npantagy-, tri-m-octogy- andtri-m-dedecacyborogine. Except for tri-mdedecomyboronine which multed at 30° C., the compounds prepared ware liquids at room temperature. Of the boroxines studied, all decomposed upon attempted distillation to split off the corresponding trialkoxyborene, (ED).B. The temperature required for the decomposition was higher than the boiling point of the trialkery borene, the difference varying from 102° for the ethyl compound to 35° for the dedecyl compound. Coupeen, in a study on trimethosyboroxine, and Lappart (25), working with trimethogy, triethogy, tri-n-proposy, triisoproposy, tri-n-butory, triscutory-, and tri-sec-but apporations, similarly found that the borowines would not distill, but decomposed to yield the alkyl orthoborate at a bath temperature higher than the boiling point of the orthoborate. The decomposition temperatures were not listed by Lappart. Lappart (25) also found that attempted distillation of the boroxine under reduced pressure caused dispreportionation to yield the orthoborate and boron trioride.

The infrared spectra for the boronines studied were obtained.

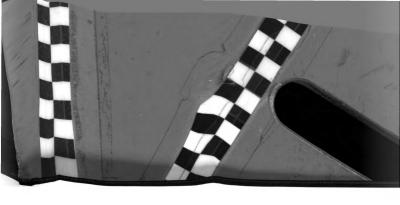
Resever, examination of the spectra indicated that the samples had

bocoms partially hydrolysed so no conclusions were made from the curves. The infrared spectra of some alkomyboromines were obtained by Lopport (25) who concluded that absorption near 720 and 735 on is of good diagnostic value for metaboric esters (boromines).

The rates of hydrolysis of the boroxines studied appeared to diminish with increasing molecular weights. The densities of the boroxines studied decreased with increasing molecular weight. The densities followed the relationship D = a + bt over the temperature range studied.

Molecular weight determinations and boron analyses showed the compounds to have the trimeric formula, (ROSO)3. This is in agreement with the data of Goubeau and Keller (16) for trimethoxyboroxine, and that of Ogle (7) for trimethoxyboroxine and tri-n-butoxyboroxine.

Lapport (25) concluded from indices of refraction that trimethoxy-, tried-n-butoxy-, triisopropary-, tried-n-butoxy-, trie



#### II. REACTION OF ARCUATIC ANDRES WITH ALKOXYBOROXINES

## Introduction

One series of reactions of alkoxyboroxines with andnes was studied to note whether the reactions of these types of compounds were similar to the reactions of amines and alkyl orthoborates. In the review by Lappert (h) a number of references on the reactions of amines with alkyl orthoborates are cited. However, the literature lacks any reports on the behavior of amines and alkoxyboroxines. Hence this study of the reactions of trialkoxyboroxines (trinsthoxy-, trishoxy-, tri-n-propoxy-, tri-n-butoxy-, tri-sec-butoxy-, triiscoutoxy-, tri-n-pentoxy-, tri-n-cotoxy-, and tri-n-dodecoxyboroxine) with the aromatic amines (amiline, p-aminocotoxy-) are tri-n-dodecoxyboroxine) with the aromatic amines (amiline, p-aminocotoxy-) are tri-n-dodecoxyboroxine) with the aromatic amines (amiline, p-aminocotoxy-) and tri-n-dodecoxyboroxine) with the aromatic amines (amiline, p-aminocotoxy-) aminocotoxy-, and tri-n-dodecoxyboroxine) with the aromatic amines (amiline, p-aminocotoxy-) aminocotoxy-, aminoc

Addition of an other solution of the antline to an access of the boroxine in other solution at room temperature produced a precipitate which suggested Structure I.

Compounds of this type have been propered from sailine and six substituted sailines and from two arounds dismines. Tri-mothony- and triothony-boronine have been successfully used as a reagent, but tri-n-property, tri-n-butony, tri-sec-butony, triisobutony, tri-n-pentony, tri-n-cetony, and tri-n-dedecomploresime yield no reaction products under identical conditions. Diszone and benzene are adequate substitutes for the other solvent in this reaction; acctone and carbon tetrachloride can be used with a decrease in yield.

Evidence that the product has Structure I may be summarized as follows:

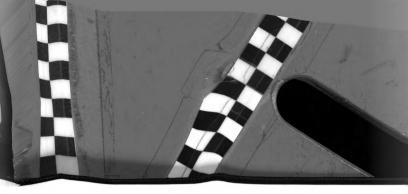
- 1. That the expirical formula is correct has been established by smalysis of seven smilines for boron, hydrogon, nitrogen, and chlorine (when present) and analysis of products from reactions of tristhoxyboroxine with the same smilines for boron alone.

  These smalyses have also established that the product is a "monomer" rather than a polymor of smiline and the boroxine.
- 2. That the borowine is not being decomposed to the allylorthoborate, which in turn reacts with the smiline, is shown by the
  fact that smiline does not form a precipitate with the orthoborates. It was also shown that when borom trioxide is added
  to an other solution of smiling, no reaction occurs.
- 3. That the amiline is not altered beyond losing the two hydrogen stoms bonded to the nitrogen is shown by the fact that hydrolysis of the product with hot potessium hydroxide permits quantitative recovery of the amiline.

Compared of this type have been prepared from million and ofer and advantable to a respectively and continues and from the expective electron. Interstance and from an accordance and accordance accordance and accordance acco

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- 3. Then the entities to not altered beyond leading the tree indentities about bonded to the military as them by the first time that indentities as the first product with het potentials plantities as the entitles.

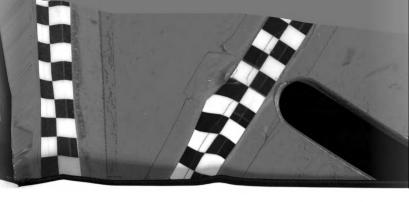


h. That a mitrogen-boron band is formed is suggested by the fact that displacement reactions of the type:

are known (63,64) to occur under conditions similar to those used in this reaction. The reaction say be represented by the equation:

Qualike polymers are produced from amiline and the borozine if the mole ratio of the reactants is near unity and if the reaction mixture is refluxed for several hours. Polymers are also obtained in the absence of a solvent by constantly stirring a mixture of the reactants at room temperature. The material prepared in the absence of solvent is a viscous oil which swells to a gum when solvent is added. The repeating unit in the polymer appears to have the Structure II.

This assumption is based primarily on an analysis of boron in the polymer. These polymers are less susceptible to noisture than the boronine.



# Experimental

19

#### Preparation of the Boroxines

Trinsthage, trientage, trien-propage, trien-butage, triescobutage, triisobutage, trien-pentage, trien-octage, and triendedecomparatine were propared by the method doubeau and Keller (16) used to propare trinsthamptoraxine, that of reacting boric ambidride and the corresponding allyl orthoborate. Their proparation is described in the section on allowyboraxines (Section I, page 27).

#### Formation of Monomer

Solutions of the amilians listed in Table 12 were prepared by dissolving 0.01 mole of the amilian in 50 ml. of ambydrous other; the boronine solutions were prepared by dissolving 0.04 mole of the boronine in 50 ml. of ambydrous ether. Flasks used for this purpose were protected from atmospheric water vapor by drying tubes containing CaCl<sub>2</sub>. A white precipitate formed immediately upon addition of the amilian solution to the boronine solution. The mixture was shaken for 3-5 minutes, the precipitate was allowed to settle and was filtered rapidly through a Buchner furnal. The precipitate was weaked several times with other, dried in a stream of warm dry air and stored in a vacuum desiceator.

In a typical experiment, 1.07 g. (0.01 mole) of p-toluidine dissolved in 50 ml. of ether was added to 6.96 g. (0.04 mole) of trimsthoxy-boroxine in 50 ml. of other. This produced 3.5 g. (0.009 mole) of N,N-bis(dimethoxyboroxiny1)p-toluidine. Other results are given in Table 12.

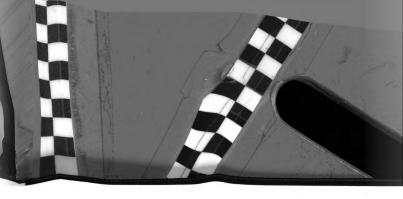
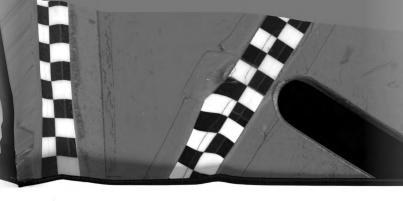


TABLE 12
YIELDS IN REACTIONS OF ANILINES WITH BOROXINES

Aniline Used	Holes Aniline Teken	Moles Compound With (CH <sub>3</sub> CBO) <sub>3</sub>	Moles Compound With (CgHsOBO):
Amiline	0.010	0.0088	0.0068
p-Chloromiline	0.010	0.0080	0.0057
p-Anisidine	0.010	0.0092	0.0071
p-Aminobemacie Acid	0.010	0.0081	0.0060
p-Nitrosniline	0.010	0.0033	
p-Aminoacetophenone	0.010	0.0040	0.00214



The same reaction was also studied (antiline plus boroxine) with discusse, bensame, acctome, and carbon tetrachloride instead of disthylations.

51.

In reactions of diamines the noise ratio of boronine to seine was eight to one.

### Formation of Polymers

The procedure outlined above was used by Lippincott and Ogle (65) in preparing polymers of smiline and trimethoxyboroxine except that the mole ratio of reactants was made unity and the reaction mixture was refluxed for six hours. Ether or acetone served as a solvent. During the raffux pariod the white precipitate initially formed disappeared and a brown gum-like material formed in its place.

The polymer was prepared by Lippincott and Ogle (65) without use of a solvent by adding smiline to the boronine at room temperature and stirring the mixture for 30 minutes. Considerable heat was evolved during this time and a viscous brown oil resulted. Analysis of the oil for boron gave 14,39% calculated for the material represented by Structure II, 14.50%. Addition of the oil to other produced a gun-like material similar to that obtained if the reaction was carried out in a solvent.

#### Identification of N.N-bis(dialkocyberoginyl)smilines

Hydrolysis of 0.4 g. of the product obtained from reacting trimethoxyboroxine and p-toluidine with 1 N KCH, extracting with other and evaporating the other extract resulted in recovery of 0.11 g. p-toluidine,



calculated for the material represented by Structure I, 0.12 g. Similar results (Table 13) were obtained for the other amiline compounds.

52

Melting points of the reaction products were not sharp. The heating decomposed the compounds to give unidentified products.

The boron analyses were accomplished by the method of Kolthoff and Sandell (62). Tables 14 and 15 indicate the results of analyses of the fourteen smilldes prepared by this reaction.

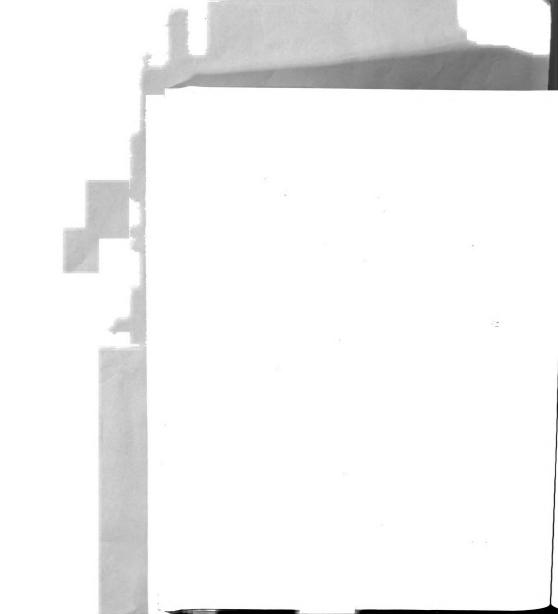
Minro analyses for carbon, hydrogen, nitrogen, and chlorine were performed by Clark Minromelytical Leboratory. The carbon analyses were erratic and unreliable even though  $V_2 \rho_3$  was used in the conjustion tubes. Table 11, summarises the hydrogen, nitrogen, and chlorine analyses for six antilides prepared from trinsthocyberoxine.

Attempts to determine the nolecular weight shullioscopically and cryoscopically were unsuccessful due to the extreme insolubility of the sailine compounds.

The infrared spectra of the compounds were obtained. However, smallysis of the spectra indicated that the compounds had become partially hydrolyzed. Thus no conclusions about the structure of the compounds could be made from the spectra.

#### Resettion of Alleylorthoborates and Boron Trickide with Amilias

In order to determine if trimethyl borate would form a precipitate with smiline, a solution containing 0.01 mole of smiline in 50 ml. of other was added to a solution of 0.01 mole of trimethylborate in 50 ml. of other. No visible reaction occurred. The experiment was altered,



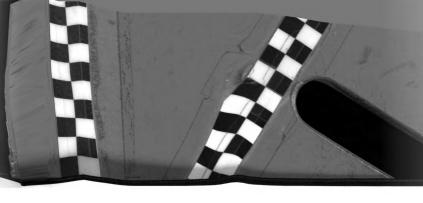


Table 13
REFULTS OF HEDROLYSIS OF N.N-bis(DIALKOXIBOROXIN'IL)ANILINES

Andline in Compound	Holes Compound Extrolysed	Moles Aniline Recovered
Ariline	0.0029	0.0028
p-Chlorosniline	0.0022	0.0022
p-Anisidine	0.0018	0.0014
p-Aminobenzoic Acid	0.002),	0.002),
-Hitromiline	0.0017	0.0018
-Aminosostophenone	0.0015	0.0012
p-Toluidine	0.0011	0.0010

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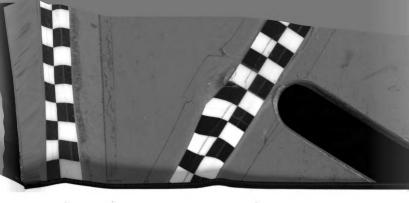
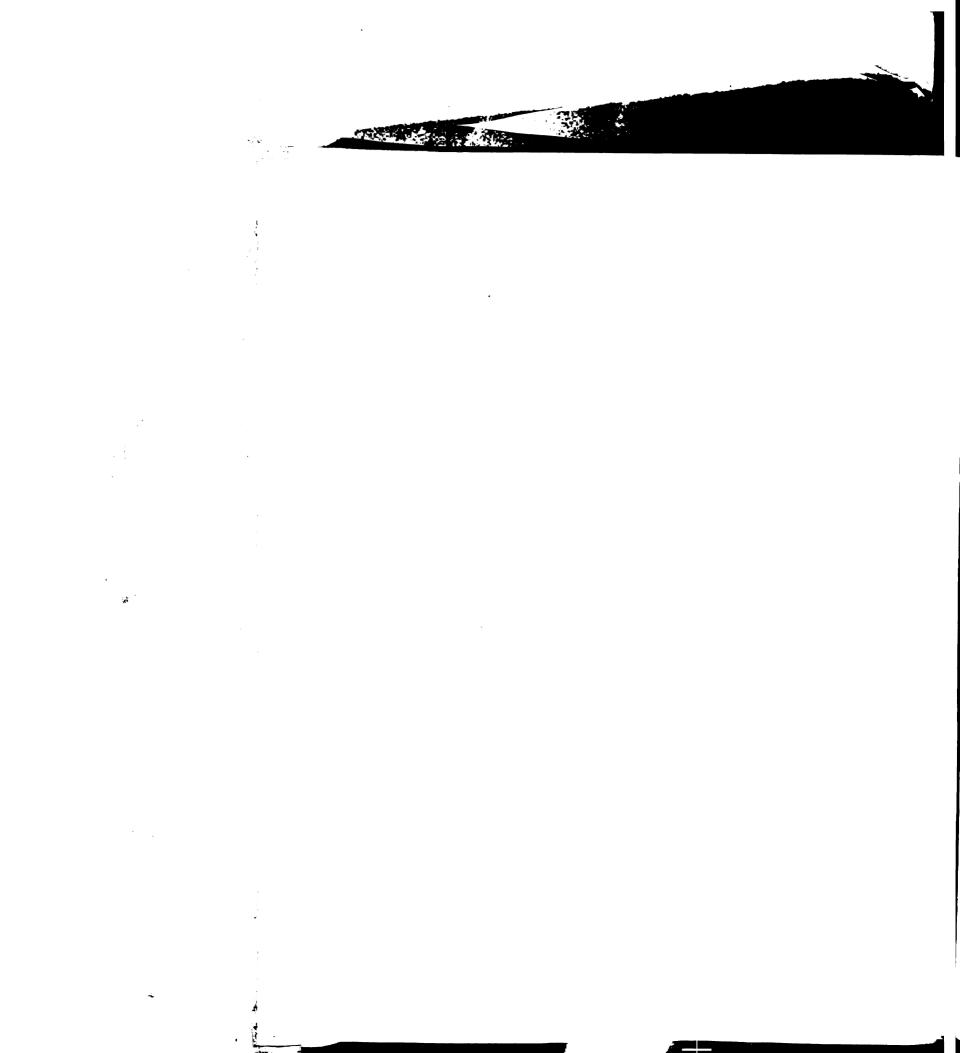


Table 14
RESULTS OF ANALYSES OF N.N-Big (DIRETHOXYBOROXDIYL)ANILINES

totatus Wood	Found Composition Calculated							
Aniline Used	В	H	N	CI.	В	H	N	Cl
Antline	17.30 17.51				17.24			
p-Chlorosniline	15.80 15.07	3.85 3.59	3.50 3.18	7.36	15.79	3.90	3.41	8.6
p-Anisidina	16.41 16.42				15.91	4.68	3.45	
p-Aminobenzoic Acid	15.07 15.24				15.43	4.05	3.35	
p-Hitrocniline	15.24 15.16	4.01			15.40	3.80	6.65	
p-Ajinoacetophenone	14.26	4.22			15.50	4.54	3.43	
p-Tolaidine <sup>a</sup>	16.50	4.85			16.61	4.90	3.58	

<sup>&</sup>lt;sup>2</sup>Resortion solvent dimmns—16.60 and 16.38% B; reaction solvent bensons—16.54 and 16.15% B.



BORON ANALYSIS OF N.H-B1s (DIDINIONONONINYL)ANILINIS

	Per Cart Boron	
Aniline Used	Found	Calculated
Aniline	15.03 15.04	15.01
p-Gilorosniline	13.68 13.64	13.09
p-Amisidine	14.04 14.18	14.03
p-Auinoecetophenone	13.77 13.74	13.63
p-Aminobossois Acid	13.28 13.64	13.62
p-Toluidine	14.86 14.95	14.53

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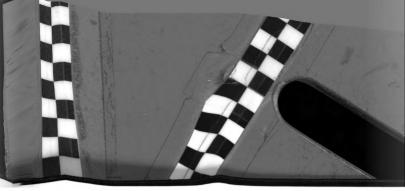


TABLE 16

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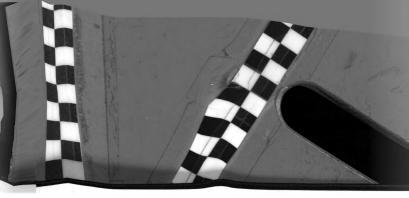
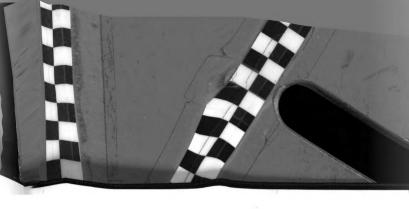


TABLE 17 BENZIDINE CO.POTED

# For R = CH,

Per Cent	Calc'd (I)	Celc'd (II)	Calc'd (III)	Found
B H H	17.29 3.74 4.27	15.98 4.60 4.44	13.88 6.00 4.71	16.10, 16.15 3.49, 3.76 4.20, 3.91
		For R =	C <sub>e</sub> H <sub>5</sub>	
Per Cent	Cale'd (I)	Cale'd (II)	Calc'd (III)	Found
B N H	15.05 3.25 5.57	13.84 3.98 5.55	11.82 5.11 5.65	14.02, 14.10 3.75, 3.79 4.41, 4.64

AL MON.



using 3:1, 12:1, and 1:3 retice of borsts to smiline, but no precipitate formed. Similar negative results were obtained with trickled borsts.

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To check the possibility of smiline reacting with boron trickide

0.01 male of smiline in 50 ml. of other was added to a mixture of 0.01

male of boron trickide and 50 ml. of other. No visible reaction occurred.

The white solid was recovered by filtration and dried in a vacuum

dessicator. Analysis of the white solid for boron showed it to be boron

trickide. The experiment was altered using 611, 311, and 113 ratios

of boron trickide to amiline, but the boron trickide was recovered

quantitatively in each case.

Since aniline will not form a precipitate with trimethyl borate, triethylborate, or boron trioxide, it is assumed that the compounds formed in this study are not the result of decomposition of the boroxine to the allyl orthoborate and boron trioxide.

### Hydrolysis of the Product of Phenylandianina and Trimsthocoborozina

A hydrolysis reaction was carried out to determine if the amine could be recovered from the product of phenylenediamine and trimethoxyboroxine.

Hydrolysis of 0.44 g. of the product obtained from reacting trimethocyberoxine and phenylemedicaine as above with 1 N. KCH, extraction with other and evaporation of the other extract gave 0.11 g. phenylemedicains (calculated for II, 0.096 g.). neing 1st, 18st, and 1st retien of bounds to entition, but no precipitates founds. Similar negative results wise extended becomes

To check the possibility of waller res scientist with beres tricking of 0.01.

O.C. who of malline is 50 ml. of which was added to a michany of 0.01 was a far and the scientist comment.

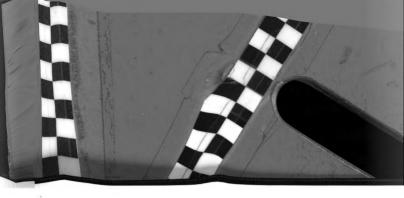
The white walle was recognized by Cliterician and dried in a vertical descionance of the white walle for bores and or to be bored interested in the comment. The emperiors was altered and for bores and of 1.1 resides of bores triangled to emiliar, has the bores triangled was recognized as the contract of the contract of the same triangled was recognized as the contract of the contract

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A hydrolysta constant was careful out to determine if the hydrocould be recovered from the present of physicarchicales and technicaryberedon.

indesignate at 0.1d. g. of the product obsciled from mentions of the season and planetaries of the characteristic or chosen after 1 H. 200, activations at the cities and expensions of the characteristic or the characteristics of the cities achieve achieve achieves (coloraboted for II. 0.096 g.).



## Discussion

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When aromatic amines and, allowyboroxines are reacted, either monomeric (Structure II) or polymeric (Structure III) (see pages 16 and 18) products are obtained. The reaction by which the monomer is formed is very rapid; polymer formation is apparently considerably slower. Both reactions are exchanged. With trinsthocyboroxine the yields are nearly quantitative, although very week bases such as p-nitroaniline give lower yields. With triethocyboroxine these yields are reduced by approximately one-third; p-mitroaniline gives no product at all.

The products obtained from the reactions of the dismines are apparently mixtures containing both three and four dislikes/borowinyl groups attached to one molecule of dismine.

The mechanism undoubtedly involves attack of the amine nitrogen on a boron atom followed by a proton transfer from nitrogen to caygen and subsequent formation of alcohol by cleavage of the boron-caygen bond. The base strength of the amine nitrogen appears to be a critical factor in the mechanism as is evidenced by the low yields for the three nitro-anilines. The decrease in reactivity caused by the change from trinsthacy-boronine to the higher honologues may be explained by the increase in steric hindrence around the boron atoms as the allowy groups become larger.

# III. DENYDEATION OF CHARGEORIC ACID

# Introduction

The name "boric soid," unless otherwise qualified, refers to orthoboric soid, H<sub>2</sub>BO<sub>3</sub>. As is the usual case with "ortho" soids, orthoboric soid is the most highly hydrated and may lose a molecule of water to form motaboric soid, IBO<sub>2</sub>.

A survey of the literature reveals that on hosting above  $100^{\circ}$  C. orthoboric acid gradually loses water, changing to metaboric acid (66). At higher temperatures all the water is lost and ambydrous boron trickle,  $B_2O_3$ , results. Although the elder literature (67) reports a pyroboric (tetrahoric) acid,  $B_2O_4$ , X-ray and tensionstric studies (68) have shown that the dehydration from  $EDO_3$  to  $B_2O_3$  is a continuous process without the formation of any intermediates.

Phase studies (63,69) of the system  $B_2O_3-H_2O$  also show that the only stable hydrates of the oxide to be the 1-hydrate (HBO<sub>2</sub>) and the 3-hydrate (HBO<sub>3</sub>). Kracch, Horey, and Horwin (69) obtained a phase diagram for the system  $B_2O_3-H_2O$ , based on results obtained by heating mixtures in socied tubes. They found the only solid phases to be ice, orthoboric soid, and three modifications of notaboric acid:

rhombic HBO<sub>2</sub>I density, 2.136; m.p., 236° C. nonoclinic HBO<sub>2</sub>II density, 2.011; m.p., 200.9° C. orthombic HBO<sub>2</sub>III density, 1.76; m.p., 176.0° C.

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The name wheels auth, " where otherwise qualified, return to arthorous auth, H<sub>0</sub>NO<sub>2</sub>. As he the usual executive "ortho" author action, creations as an action of rates to antical as the respondent authority indicated and may less a majorale of rates. NO<sub>2</sub>.

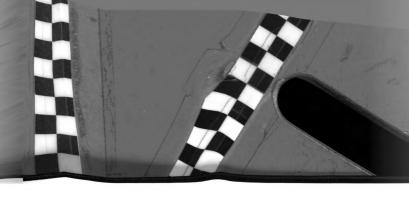
contrated and productly train their conjugat test on beautiful above 100°C.

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constitues strates (db.,Gr) of the spetce Lg2,-Lg also ther that the safeschills impleste at the cults to be the liveletan (LD1) and the frequent (mg20g). Thereby, many, and larets (Ry) observed a phase observed for two equates B<sub>2</sub>C<sub>2</sub>-t<sub>2</sub>C<sub>3</sub>, bessed on stratifier observed by insufficie infrinces of excelled below. They focus the ordy model phases to be tooy extendedly and there exists obtains at unicolouse safets

and the construction of th



Since tolurne (b.p., 110.7° C.) is often used to executope the unter produced in the esterification of orthoboric acid, it was the purpose of this investigation to study the possibility of orthoboric acid itself being dehydrated by reflucing in tolurne. It was found that the reflux mixture (tolurne plus orthoboric acid) yielded netaboric acid. Notaboric acid was also produced by refluxing orthoboric acid in beasens. In both cases the netaboric acid was identified as HBO<sub>2</sub>III.

Refluxing of orthoboric acid with sylene yielded products less hydrated than HBO<sub>2</sub>, but with no reproducible composition. A study of the relative solubilities of orthoboric acid, metaboric acid, and boron trioxide in a series of alighstic alcohols was made.

### Ecorrinantal

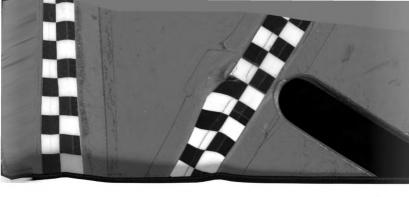
### Preparation and identification of metaboric acid

A mixture of 18.6 g. (0.3 makes) of orthoboxic acid and 200 ml. of dry tolurene were heated under reflux using a constant water separator.

After 8 hours the amount of water removed appeared to remain constant at 5 M ml. (Theoretical for H<sub>2</sub>BO<sub>2</sub> \rightarrow \text{HBO}<sub>2</sub> + H<sub>2</sub>O<sub>3</sub> 5 M ml. at H<sub>2</sub>O). The mixture was allowed to cool to room temperature, filtered through sintered glass, and the white solid washed with anhydrous chipl ether. The white solid was placed in a vectom desicostor and the desicostor pusped for 2M hours to remove any excess other. The white solid was placed in a weighing bottle (marked T<sub>2</sub>) and stored in a desicostor over CaCl<sub>2</sub>.

Boron analysis of the white solid, T<sub>2</sub>, yielded 2M.57% B (calc. for HDO<sub>2</sub>, 2M.69%). The experiment was reposted, refluxing 62 g. (1 mole) in hOO





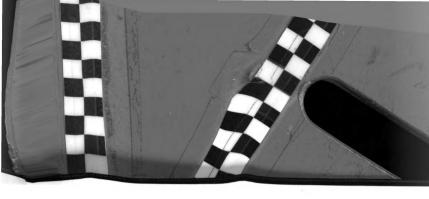
al. dry toluene for 12 hours to yield 13 al. (1 nois) of  $H_{2}0$  and hh g. (1 nois) of white solid,  $T_{2}$ , which was handled as with  $T_{1}$ . Analysis of  $T_{2}$  yielded 2h.7h2 B. It was noted that the pot temperature never rose shows  $110^{\circ}$ , nor the vapor temperature above  $108^{\circ}$  (b.p. of toluens is  $110.7^{\circ}$ ).

To establish whether a temperature below  $100^\circ$  could be used to dehydrate orthoboric sold by assectropic drying, 15.5 g. (0.25 mole) orthoboric sold was realized in 200 ml. dry beamens (b.p., 80.2). After 12 hours, the amount of water reserved was constant at h.i. al. (theoretical for  $\rm H_3 BO_3 \longrightarrow \rm HBO_3 + \rm H_3 O_1$  h.5 ml.). The white solid (B<sub>3</sub>) was handled in the same number as T<sub>1</sub> and T<sub>2</sub>. In another run, 18 ml. (1 mole) of water was runoved from 62 g. (1 mole) of orthoboric sold in h00 ml. of beamens, to yield h3.6 g. of white solid (B<sub>2</sub>). The pot temperature did not go shows  $80^\circ$  C. The solid B<sub>2</sub> was treated similarly to B<sub>1</sub>, T<sub>2</sub>, and T<sub>2</sub>. Boron analyses for B<sub>1</sub> and B<sub>2</sub> showed 2h.52 and 2h.50% B, respectively.

The melting points of metaboric acid samples  $T_1$ ,  $T_2$ ,  $E_1$ , and  $E_2$  were obtained by heating the compounds in scaled multing point tubes. The samples multad sharply at  $175^\circ$ ,  $175^\circ$ ,  $175^\circ$ , and  $176^\circ$ , respectively. The multing point of  $180_2$ III is  $176^\circ \pm 0.2^\circ$  C.

To determine whether prolonged heating would further dehydrate the metaboric acid, 12.4 g. (0.2 nois) of orthoboric acid was placed in each of two flacks containing 200 ml. of tolume and 200 ml. of bensome, respectively. The mixtures were refluxed with constant water removal for 72 hours. In both cases the final volume of water collected, 3.6 ml. (0.2 nois) had been removed after 6-6 hours. Analyses of the solid

To declarate the control products the state and declarate despites the control declarate to the control of the control of the state and the titles the control of the state the control of the state and the state a



products indicated 24.58% and 24.65% B (cale. for HBO<sub>2</sub>, 24.69%), for samples from the bennens and toluens reactions, respectively. Both samples malted at 175° (m.p. of HBO<sub>2</sub>HH, 176°).

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To determine if a higher building liquid then tolume would cause further dehydration, 18.6 g. (0.3 sole) of orthoboric acid was refluxed for 8 hours in 200 ml. sylame. The volume of water removed was 7.0 ml.

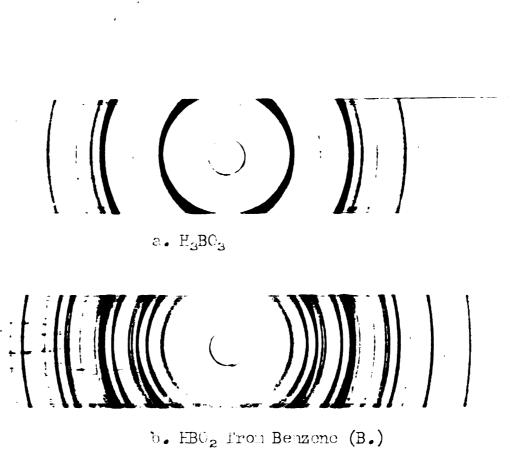
Boron analysis of the dried solid product indicated 26.045 B. (Calculated for H<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, 27.51%). Other runs using sylame as the solvent gave products having 28.40, 29.40, and 29.52% boron. This indicates that sylame cannot be used to dehydrate orthoboric acid to a defininte composition.

In another experiment, 11 g. (0.25 mole) of metaboric acid was radiated in xylene for 12 hours with constant removal of the water (1.3 ml.). Analysis of the dried product indicated 29 AS B.

K-ray diffraction patterns were obtained for orthoboric soid, note-boric soid, boron trioxide, and the xylens dehydration product. Samples were proposed by grinding and packing the resulting poster carefully into a 0.03 ms. glass capillary. The capillary was scaled with a match flame to give a sample tube of about one-half inch length. This tube was then mounted in a Phillips Debye-Schenzer type, 11.1 cm., camera. After alignment the camera was loaded with Kodak No-Screen type film which had been cut and punched to fit the camera. The camera was then placed on the Novelco K-ray undt for exposure. All exposures were for 6 hours at 35 KV and 16 ms, using copper K-a radiation.

The patterns obtained from the various samples are included (Fig. 1) along with a list of "d" spacings and the relative intensities of the lines of the X-ray patterns (Table 18).









 $\dot{\textbf{u}}$  . Xylene Dehydration Product of  $\textbf{E}_{\mathbf{3}}\textbf{B}\textbf{C}_{\mathbf{3}}$ 



e. B<sub>2</sub>0<sub>3</sub>

Figure 1. X-ray Powder Diagrams for H<sub>3</sub>BO<sub>3</sub>, HBO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub>, and Xylene Dehydration Product of H<sub>3</sub>BC<sub>8</sub>.



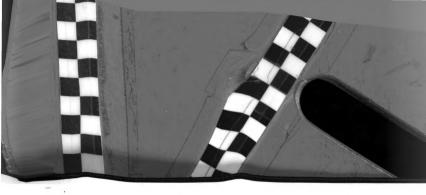


TABLE 18

VALUES FROM X-RAY PATTERS FOR H<sub>3</sub>BO<sub>3</sub>, HBO<sub>3</sub>, B<sub>3</sub>O<sub>3</sub>, AND
XXLERE DEREDRATION PROUNT OF H<sub>3</sub>BO<sub>3</sub>

de Values	Intensity	"d" Values	Intensit
6.05		H <sub>3</sub> BO <sub>3</sub> 2.25	•
4.80	w	2.24	s va
4.60	÷	2.16	W
4-21		2.10	8
1.05	w	2.04	W
1.05 3.52 3.13 3.102 2.95 2.91 2.85 2.73	YYW	1.98	VW
3.15	VVV	1.95	AAR
3.19	vvs	1.90	AAM
3.02	v	1.69	VVW
9.05	VS	7.64	VVV
2 .01.	VS	1.50	
2.85		1.59 1.51 1.47 1.40	VVV
2.73	YVW	1.1.7	VW
2.66		1.40	VVV
2.57	v	1.36	VVW
2.50	v	1.175	WW
2.29	÷		****
		HBO (Ta)	
6.05	VS	2.19	v
4.92	YS	2.16	w
4.40	VS	2.07	WW
4.40 4.40 4.12		2.02	WW
h ~00		1.96 1.86	
3.82	8	1.86	w
3.82 3.70	w	1.79	vw
345	VE	1.73	WW
3.19	VS	1.68	w
3.12	VVS	1.66	VV
2.99	W	1.60	VVW
3.45 3.19 3.12 2.99 2.91	AAM	1.56	w
2.70	w	1.34	VVW
2.51		1.188	VVV
2.46	8	1.172	WW
2.51 2.46 2.38 2.25	w	1.15	W

Continued

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1.15		Albert.	8	2.66
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QL   QL   QL   QL   QL   QL   QL   QL	MAA	Chief		2,50
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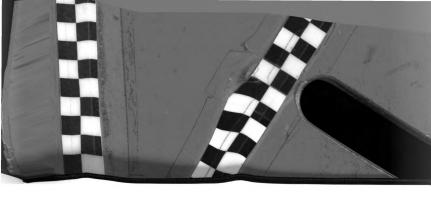


TABLE 18 - Continued

"d" Values	Intensity	"d" Values	Intensity
	H30 <sub>2</sub> (B	2)	****
6.07	VS	2.06	VVW
4.93	VS	2.01	AAM
4.40	78	1.96	8
4.13	•	1.87	v
4.00	•	1.86	VVW
3.82		1.79	AM
3.70	V	1.73	VVW
3.46	va	1.68	w
3.20	VS	1.66	W
3.12	vvs	1.64	VVV
2.98	*	1.61	VVW
2.90	VVV	1.56	w
2.78	AAA	1.50 1.46 1.36 1.23	VVW
2.70	w	1.46	AAM
2.51	•	1.36	· VVW
2 410		1.23	AAA
2.38	w	1.21	VVW
2.32	VW	1.188	AAM
2.25		1.17	VVW
2.19	¥	1.15	w
2.16	٧		
	B <sub>2</sub> O	2	
6.05	ve	2.25	w
3.19	VVS	2.10	VVW
2.88	W	1.69	VVW
2.57	AAM	1.59	VVW
	HaBOa Dahydra	ted in Xylene	
6.05	vs	1.68	VVW
3.28	VVS	1.59	VVW
2.90	v	1.51	VVW
2.25		1.39	VVW
2.10	VVW	1.17	VVW
2.02	VW		

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Comparison of the "d" values and relative intensities of the lines of the X-ray patterns indicate that the dehydration of orthoboric acid in bemsene and in toluene yielded the same form of metaboric acid. Since the purpose of the X-ray study was a qualitative comparison of the two samples, and also since the crystal structure of the orthorhombic RBO\_XIII is known (65,69), no further work was done with the X-ray patterns.

Density measurements of metaboric acid were made at 25.00 ± 0.02°. A weight pyenometer with a thermometer and a small capillary side-erm was used. The pyonometer was calibrated with radistilled water. The toluene used was the middle one-third of freshly distilled CP toluene. The density of the toluene was determined, using the calibrated pyonometer. For the density determination of the solid metaboric soid, the solid sample was weighed into the clean dry pycnometer. Toluene was placed over the solid, and the pycnosster was placed in a vacuum system to remove any occluded bubbles. After the toluene was allowed to boil at least a half hour at room temperature, the pyunometer was removed from the vacuum dessicator, filled completely with tolurne, and placed in a thermostated bath at 25.00 ± 0.02° C. The time necessary for establishment of thermal equilibrium was determined from the time it took for the temperature in the pyonometer to equal the temperature in the bath. This time (15 to 30 minutes) was quadrupled to guarantee thermal equilibrium. Accordingly, after two hours the prenometer was removed from the bath, capped, cooled in a stream of cold water and placed in

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Comparison of the Car values and industries intensibles of the lines and orientation of the lines and in because and in telescopy yielded the energy of make of make the purpose of the lines of the lines of the two employ, and (dee where two expects at the orientalistic and the orientalistic and the orientalistic and the orientalistic and the beam (16,67), as the bear west and done with the Levy publishers.

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the balance case for weighing. Densities were calculated by the following formula:

de - density of the solid

dsolv - density of the solvent

ws - weight of the solid sample

wantt - weight of the solid plus solvent contained in the pythnometer

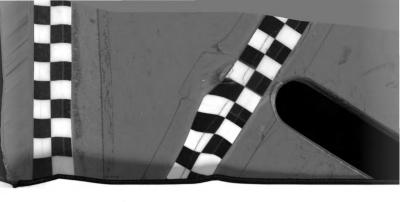
voyc - volume of the pychnometer

Heasurements were made on the metaboric acid prepared by dehydration in toluene ( $T_1$  and  $T_2$ ) and in beasene ( $B_1$  and  $B_2$ ). The densities (g/cc) are:  $B_1$ , 1.77;  $B_2$ , 1.78;  $T_1$ , 1.78;  $T_2$ , 1.77. All the density determinations agree with the known value of 1.78 for HBO<sub>2</sub>(III) (69).

# Schubilities of Orthoboric Acid, Nataboric Acid, and Boron Trioxide in Alcohols

In order to determine the relative solubilities of orthoboric acid, metaboric, and boron trickide in a number of alcohols (methyl-, ethyl-, n-propyl-, n-butyl-, n-anyl-, and n-hoptyl alcohol), 20.0 g. of the respective boron compound was added to 50 ml. at the embydrous alcohol in mixing cylinders equipped with ground glass stoppers. Duplicate mixtures were propared for each boron compound and alcohol mixture. Equilibration was effected by mechanical shaking in horizontal position in a constant temperature both maintained at 25.00 ± 0.02°. After shaking had continued for 21 hours, one of each different mixture was

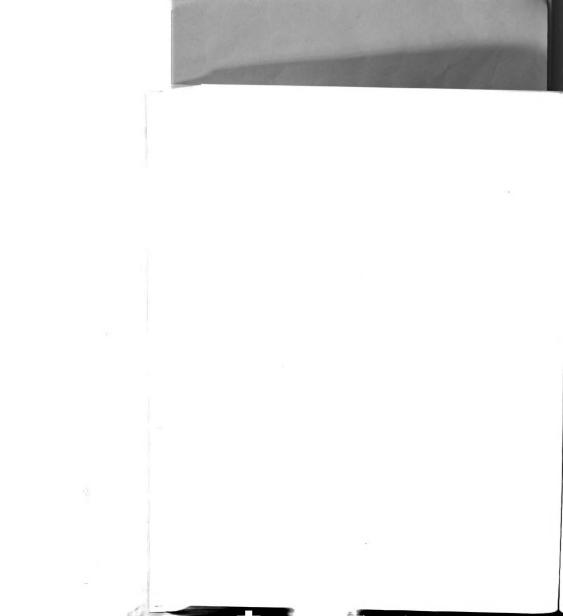




filtered through sintered glass. The solid residue was washed with snivdrous other and placed in a vacuum dessicator to remove the volatile other. Samples of the liquid were analyzed for boron by dissolving in water. adding namnitol, and titrating with standard base. The duplicate mixture of each was allowed to shake for an additional 2h hours. Analysis of the liquid phase of each showed that solubility was complete in the first 2h hours. The results of the analysis of the liquid phases (that is, the solubilities) are given in Table 19. For comparison the solubilities are listed as moles of boron, grams of boron, and grams of boron compound, dissolved in 100 ml. of solution. The results of the boron analyses of the respective solid residues are given in Table 20. Since the dissolution of the boron compound is probably through esterification by the alcohol, water is one of the products. That some of the undissolved solute (in the case of the BaOa and HBOa) is becoming hydrated is clearly indicated by comparing the results in Table 20 with the calculated values for H2BO3, HBO2, and B2O3 for per cent B. Further runs using 50 ml. of alcohol were made in which the moles of B in the solute was held constant. These salubilities are given in Table 21. (Included in Table 21 are the HaBOa results from the previous runs.)

#### Discussion

The results of this study show that metaboric acid,  $H_0B_0$ , can be prepared by dehydration of orthoboric acid,  $H_0BO_0$ , by refluxing in bemans or tobians with a constant unter separator. The metaboric acid prepared here is of the form  $H_0BO_0HII$ . It is known that the  $B_0O_0^{-\omega^2}$  ion



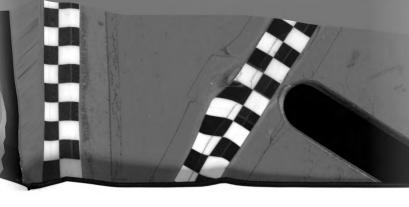


Table 19  $\hbox{ Scrubilities of $H_2BO_2$, $HBO_2$, $ABD $B_2O_3$ with constant weight of scribes }$ 

Solvent	Solute	Solubil Moles of B	ity (per 10	O ml. solution) Grams of B Compou
Cii <sub>a</sub> OH	20.0 g. HaB0a	0.307	3.32	19.0 g. H <sub>2</sub> BO <sub>2</sub>
CHACH	20.0 g. HBO.	0.511	5.85	23.7 g. HBO
CH3 CH	20.0 g. B <sub>2</sub> 0 <sub>3</sub>	0.595	6.42	41.4 g. B <sub>2</sub> 0 <sub>3</sub>
C <sub>2</sub> H <sub>3</sub> CH	20.0 g. H <sub>3</sub> BO <sub>3</sub>	0.151	1.54	9.32 g. H <sub>3</sub> BO <sub>3</sub>
C <sub>a</sub> H <sub>s</sub> OH	20.0 g. 180g	0.388	4.19	17.0 g. HBO2
C <sub>a</sub> H <sub>a</sub> OH	20.0 g. B <sub>2</sub> 0 <sub>3</sub>	01197	5.36	34.6 g. B <sub>2</sub> 0 <sub>3</sub>
n-C <sub>2</sub> H <sub>2</sub> OH	20.0 g. H <sub>3</sub> B0 <sub>3</sub>	0.080	0.869	5.25 g. H <sub>3</sub> BO <sub>3</sub>
n-CoHoCH	20.0 g. 130g	0.319	3.45	14.0 g. 180g
n-C <sub>2</sub> H <sub>7</sub> CH	20.0 g. Bg03	0.466	5.03	32.4 g. B <sub>2</sub> 0 <sub>3</sub>
n-C <sub>4</sub> H <sub>9</sub> CH	20.0 g. H <sub>3</sub> B0 <sub>3</sub>	0.0721	0.784	4.73 g. HaBOa
n-C <sub>4</sub> H <sub>0</sub> CH	20.0 g. HBO2	0.295	3.19	12.9 g. HBO2
n-C <sub>o</sub> H <sub>o</sub> OH	20.0 g. B <sub>2</sub> 03	0.434	4.68	30.2 g. B <sub>2</sub> 0 <sub>3</sub>
n-C <sub>o</sub> H <sub>23</sub> OH	20.0 g. HaBOs	0.0515	0.589	3.37 g. H <sub>3</sub> B0 <sub>3</sub>
n-C <sub>5</sub> H <sub>3,2</sub> CH	20.0 g. 190a	0.274	2.96	12.0 g. HBO
n-C <sub>o</sub> H <sub>33</sub> CH	20.0 g. B <sub>2</sub> 0 <sub>3</sub>	0.455	4.91	31.6 g. B <sub>2</sub> 0 <sub>3</sub>
n-C <sub>p</sub> H <sub>2,5</sub> OH	20.0 g. H <sub>3</sub> BO <sub>3</sub>	0.0440	0.433	2.48 g. H <sub>3</sub> BO <sub>3</sub>
n-C <sub>p</sub> H <sub>15</sub> OH	20.0 g. HBO2	0.164	1.77	7.16 g. HBO2
n-C,H <sub>10</sub> OH	20.0 g. B <sub>2</sub> 0 <sub>3</sub>	0.271	2.93	18.9 g. B <sub>2</sub> 0 <sub>3</sub>

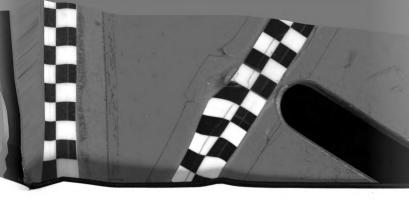


Table 20 boron analyses of the scalid phases from the scalibility studies of haboa, inducable baoa

Solvent	Percentage Boro	n for Solid Phases f	ros Each Solute B <sub>2</sub> 0 <sub>3</sub>
CEI 3 CH	17.48	17.42	17.51
C <sub>a</sub> H <sub>a</sub> CH	17.52	17.70	17.43
C <sub>3</sub> H <sub>7</sub> OH	17.40	17.39	17.44
C.HoCH	17.61	17.58	18.51
C <sub>6</sub> H <sub>33</sub> CH	17.51	17.74	18.93
C-H <sub>25</sub> OH	17.60	19.13	20.36

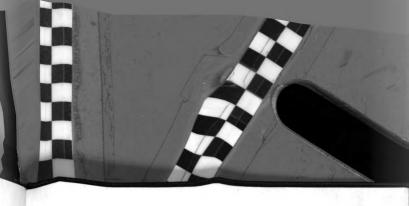
Calculate percentage boron for:

H<sub>3</sub>BO<sub>3</sub> 17.495 H<sub>3</sub>B<sub>4</sub> 21.695 H<sub>3</sub>B<sub>4</sub> 27.515 B<sub>3</sub> 31.075

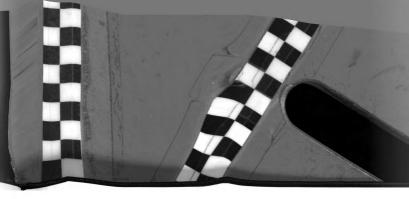
CATALOGUE TATUBRIDO THE INTRA MANDEL OFFICE AND AN COLUMNY ROSCIE.

OR STEAM

244	BORNEY AND THE	St. Self	Bellerenb
17.52	SLEE	Pale Vic	20,20
27.40	CY- Y.C	17.52	10,0,0
MAYE.	17.39	27.40	10,250
18:01	25.41	39.63	10,00
13,90	41.47	Se. PE	Dankab
20.36	1923	22.50	Blacket.
and the	20 17 195	mings bores for H	male obtains
			A Color



Mictar	Solubility (per 100 al. solution			
Solvent	Solute	Moles of B	Grans of B	Grams of B Compound
Cli <sub>3</sub> CH	20.0 g. (0.32h mole)HaBOa	0.307	3.32	19.0 g. H <sub>3</sub> BO <sub>3</sub>
CH2CH	14.2 g. (0.32h mole)hBO2	0.542	5.85	23.6 g. HBO <sub>2</sub>
CH <sup>3</sup> CH	11.3 g. (0.162 mole)Bg03	0.498	5.38	34.8 g. BgO3
C <sub>2</sub> E <sub>4</sub> OH	20.0 g. (0.32h mole)H <sub>3</sub> EO <sub>3</sub>	0.151	1.54	9.32 g. Habos
C <sub>a</sub> R <sub>S</sub> CH	14.2 g. (0.324 mole)HBO2	0.372	4.02	16.3 g. HBO <sub>2</sub>
C_H_OH	11.3 g. (0.162 mole)BgO3	0.341	3.87	23.8 g. B <sub>2</sub> 0 <sub>3</sub>
n-C <sub>e</sub> H <sub>13</sub> CH	20.0 g. (0.32k mole)HaBOa	0.055	0.589	3.37 g. H <sub>3</sub> BO <sub>3</sub>
n-C <sub>6</sub> H <sub>12</sub> CH	14.2 g. (0.32k mole)H302	0.260	2.81	14.2 g. HBO2
n-CoH <sub>13</sub> OH	11.3 g. (0.162 mole)B <sub>2</sub> O <sub>3</sub>	0.255	2.75	17.9 g. Ba03

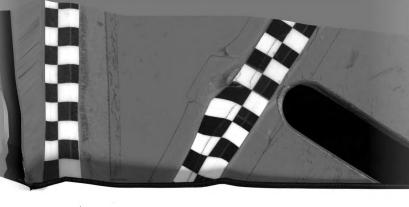


comes in potessium and sodium noteborates (11,12) and more important, that similar  $B_2O_0$  groups linked together by hydrogen bonds to form sheets, also occur in HBO\_III (70). Thus it is possible that the mechanism of esterification of orthoboric acid with an alcohol with continuous removal of the water by refluxing in toluene or beamons to form trimeric boroximes might include the formation of metaboric sold firsts

It is noted that the temperature necessary for the preparation of metaboric acid is lower than that needed for the usual thermal dehydration of orthoboric acid. This is undoubtedly due to the shifting of the equilibrium in the dehydration reaction by the constant removal of the uster.

It is noted that the netchoric acid produced in this thesis study is HHO<sub>2</sub>III. Kreeck, Morey, and Marvin (69) found that when orthoboric acid is dehydrated in open vessels at about 130° C., the product at first consists of HHO<sub>2</sub>III together with unconverted orthoboric acid; on continued heating the latter gradually disappears and the HHO<sub>2</sub>III converts to HHO<sub>2</sub>III. At this stage the dehydration stops exactly at the

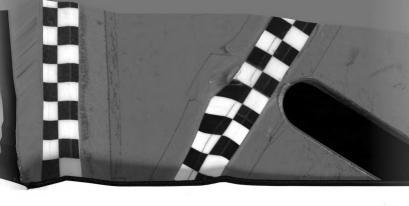




composition HBO<sub>2</sub> (so that this procedure serves as a nothed of preparation of HBO<sub>2</sub>II unless the time is excessive or the temperature is raised above  $150^\circ$  C. Under these conditions the dehydration slowly continues, yielding a highly viscous liquid whose composition lies between HBO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub>. These same vortices (69) found that when a scaled tube containing malted notaboric acid is rapidly cooled, its contents first solidify to a glass; this gradually becomes milky owing to the formation of HBO<sub>2</sub>III. On reheating this quickly crystallises to an opaque white mass malting sharply at 176.0° C. (n.p. of HBO<sub>2</sub>II is 176.0° C.).

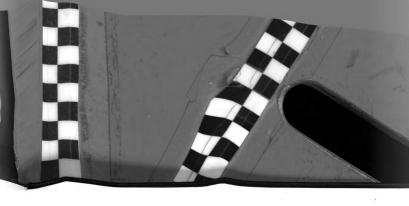
Tessici (70) produced metaboric acid by controlled heating of orthoboric acid above 100° C. in moist air at one atmosphere. Depending on the quantity of specimen, and the rate of raising the temperature, he produced either HBO\_III or a mixture of HBO\_III and HBO\_III. Tessici (70) further found that heating orthoboric acid to 150° C. for a few days would produce HBO\_III, while heating to 160-1° C. would convert the HBO\_III to HBO\_III.

The dehydration of orthoboxic acid in both toluene and bensene in this thesis study yielded  $\mathrm{HBO}_2\mathrm{III}$ , although the removal of the water appeared to be slower in the lower boiling bensene. Although other workers (69) needed a temperature above  $150^\circ$  to further dehydrate  $\mathrm{HBO}_2$  in an open vessel, this worker found that radiuxing of either  $\mathrm{H_3BO_3}$  or  $\mathrm{HBO}_3$  in xylene (b.p.,  $139^\circ$ ) would result in products having a composition between  $\mathrm{HBO}_3$  and  $\mathrm{B_2O_3}$ . This worker did not produce any tetraboric  $\mathrm{HAO}_3$   $\mathrm{H_2B_2O_3}$ , in his dehydration studies.



A comparison of the solubilities of orthoboric soid, noteboric soid, and boron trioxide in alliphatic alcohols shows a decrease in solubility with an increase in molecular weight of the alcohol (Tables 19 and 21). Analyses of the solid residues (excess boron compound) from the solubility studies showed that the excess  $\mathrm{HSO}_3$  and  $\mathrm{HgO}_3$  had become hydrated, becoming  $\mathrm{HgO}_3$  in most cases. The increased solubility of  $\mathrm{HgO}_3$  and  $\mathrm{HgO}_3$  compared to  $\mathrm{HgBO}_3$  suggests that the dissolving of these compounds in alcohols is due to esterification to form either the orthoborate or astaborate. The excess  $\mathrm{HgO}_3$  and  $\mathrm{HgO}_3$  removes the vator of esterification and retards the hydrolysis of the borate esters.





### IV. TRICYCLOHEKOXYBOROXINE

### Introduction

The method of esterification of orthoboric acid (or boron trionide) with the appropriate alcohol or phenol and removal of the water by assortroping with an inert solvent (e.g., tolmens) has been used to prepare a large number of orthoborate esters (h). In the preparation of the orthoborates at least a 3:1 mole ratio of the alcohol (or phenol) to the orthoboric acid is used to insure maximum esterification of the orthoboric acid by the reaction

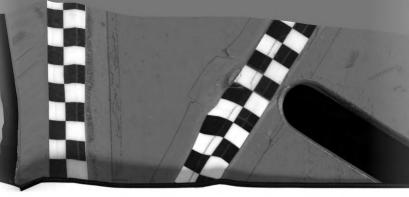
If less than a 3:1 ratio of alcohol to acid is used, maximum esterification to (20)3B is not insured and some metaborate may be produced by the reaction

O'Commor and Nace (23) found that a 2:1 mole ratio of cyclohexamol to orthoboric acid produced a mixture of cyclohexyl orthoborate and cyclohexyl metaborate

One might expect a 2:1 male ratio of alcohol to orthoboric soid to esterify as



\_



2 BOH + HaBOa --- (RO)aB-OH + 2 HaO

and then to dehydrate by

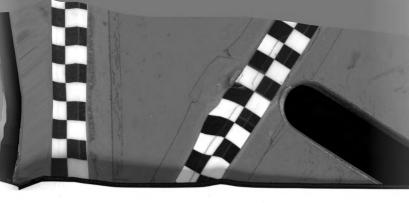
However, examples of compounds of the type (RO),B-OH or (RO),B-O-(OR), cannot be found in the literature.

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Of Commor and Nace (23) prepared 1-manthyl metaborate and cyclohesplantaborate by interaction of the appropriate alcohol and orthoboric acid in a 1:1 mole ratio; the water formed in the esterification was removed by essectropic distillation with tolmens. From the amount of water collected and the identification by boron analysis and molecular weight determination of the product, the over-all reaction was indicated to be

O'Connor and Hace suggest that the reaction is one in which the allowboric acid, ROB(CE)<sub>2</sub>, is formed first, and then it is dehydrated to form the noteborate (boratine), (ROBO)<sub>3</sub>. They could not isolate any allowyboric acid, since the dehydration yielded the boracine by the time all the boric acid had been reacted. However, O'Connor and Nace showed that if 1-manthyl metaborate was allowed to stand in the air for several hours, it adds one molar equivalent of unter to form 1-manthocyboric acid.

Since in this present study (see Section III, page 60) it was found that orthoboxic sold was dehydrated to netaboxic sold by raffixing in

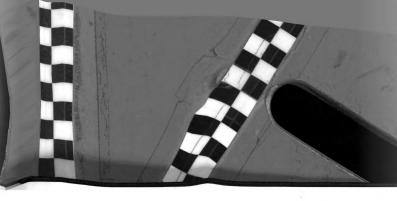


toluene or beasene, it was thought that the formation of tricyclohomorphoroxine might be carried out by the estarification of metaboric acid, RCBO, thus eliminating the intermediate RCB(CH)<sub>2</sub>. To learn more about the mechanism, attempts to prepare tricyclohomorphoroxine,  $(C_0H_{12}CBO)_3$ , by reacting cyclohomorph with orthoboric acid, metaboric acid, and boron tricxide were made.

Tricyclohecocyboroxine is a crystelline solid (m.p., 165° C.) and may be crystellised from tolumes solutions, if the solutions are sufficiently concentrated. Thus tricyclohecocyborone was chosen as a convenient orthoborate to react with orthoborae acid, metaboric acid, and boron trickide in attempts to prepare the boroxine. Tricyclohecocyboroxine was obtained in the reactions involving orthoborae and metaboric acids, but no reaction occurred with the boron trickide.

Since Schiff (13) found that ethanol reacted with othyl metaborate to form the orthoborate, it was thought that cyclohomous would react with tricyclohomomyboracine to form tricyclohomomyborane. This assumption was correct, as the reaction

went to completion with the removal of the water by assotroping with toluene.



# Experimental

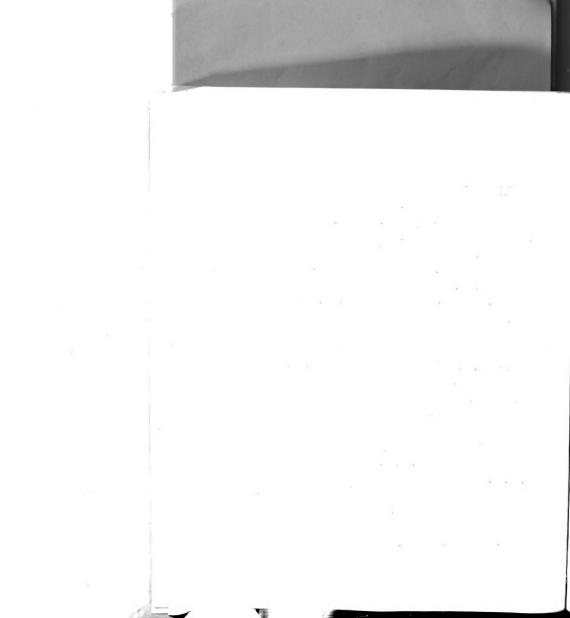
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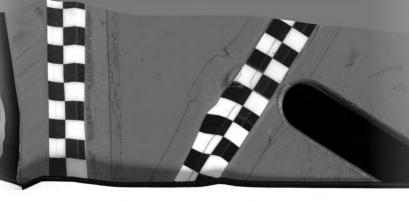
## Proparation of Triovolchemosyboronine by Resetting Orthoboric Acid with Triovolchemosyborone Dissolved in Toluene

Tricyclohexceptoreme (15.h g., 0.05 mole) was discolved in 200 ml. of dry tolmens in a round-botton flask. Solid orthoboric acid (6.2 g., 0.10 mole) was added to the flask. The mixture was refluxed with constant stirring, using a constant water separator to remove the water produced in the reaction. After refluxing for 9 hours a clear solution resulted and 2.7 ml. of water had been removed (Theoretical for  $(C_0B_{11}O_0)_3 + 2 E_0BO_3 \longrightarrow (C_0B_{11}O_0)_3 + 3 E_0O_2$ . 7 ml. of water). About 125 ml. of the tolmens was distilled off and the remaining solution allowed to cook to room temperature, whereupon a white solid crystallized. The solid was filtered and dried at  $100^{\circ}$  C. (2 ma.) for 3 hours. The product was 17.2 g., 915 yield calculated as  $(C_0B_{11}O_0)_3$ . The white solid malted at  $100^{\circ}$  C. Boron analysis gave results of 8.705 B (Theoretical, 8.625 B for  $(C_0B_{11}O_0)_3$ ). The molecular weight, determined shullioscopically in because, was 30k (Theoretical for  $(C_0B_{11}O_0)_3$ , 378).

### Preparation of Triovelehemory/corogins by Reacting Metaboric Acid with Triovelehemory/corona Dissolved in Tolumna

Tricyclohemmyborene (15.1 g., 0.05 mole) and motaboric acid (1.1 g., 0.60 mole) were reacted in the same manner as the preceding reaction with the substitution of noteboric acid for orthoboric acid. After 6 hours of refluxing, 0.9 ml. of water had been removed, and a clear solution resulted (theoretical for  $(C_0H_{11}O)_{38} + 2iBO_{3} \longrightarrow (ROBO)_{3} + H_{2}O$ , 0.9 ml. of water). The product was isolated and handled





as in the metaboric acid experiment. Analytical results for the white solid (m.p. 165-167°) were 8.55% B, and molecular weight, 371 (calculated for tricyalchemogyboromines 8.62% B, molecular weight of 378).

## Attempted Preparation of Tricyclohogosyborosine by Addition of Boron Tricyclohogosyborosis Dissolved in Toluone

Tricyclohomomyborene (15.4 g., 0.05 mole) was dissolved in 200 ml. of dry toluens in a round-bottom finsk. Diboron trickide (3.5 g., 0.05 mole) was added to the flask with no noticeable dissolution. The mixture was refluxed for 48 hours, at which time the boron trickide appeared appearently unreacted. The white solid was filtered, washed with anywhous ether, and dried at room temperature under vacuo. The dry solid weighed 3.5 g. Boron analysis of the white solid showed 30.6% B (calculated for  $B_{\rm g}\theta_{\rm a}$ , 31.0% B). The experiment was repeated with dry xylens as the solvent with the same results.

# Preparation of Triaveloheses boron by Beacting Cycloheses with Orthoboric Acid, Noteboric Acid and Boron Prioride

 Cyclohesemol and orthoborte acid (the method of O'Comnor and Nace (23)).

A mixture of 25.0 g. (0.25 mole) of cyclohexenol, 15.5 g. (0.25 mole) of orthoboric acid, and 100 ml. of dry toluene was heated under reflux using a constant water separator and constant stirring. After 3 hours all the boric acid had reacted yielding a clear solution and 8.9 ml. of water (theoretical for 3  $C_0H_{12}CH + 3 H_0BO_3 \longrightarrow (C_0H_{12}CHO)_3 + 6 H_0O_9$ . 9.0 ml. of water). About 50 ml. of the toluene was reasoned by distillation and the remaining solution allowed to cool to room

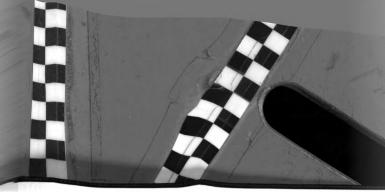


temperature, whereupon a white solid crystallized. The solid was filtered and dried at 100° C. (2 mm.) for 3 hours. The solid solid solid at 163-166° C. The yield was 29.2 g. (92.7% yield as (C#31020)3). Boron analysis of the compound gave 3.70% B (theoretical, 3.62%), the solidcular weight, determined solidizecopically in bonzene, was 368 (theoretical, 373).

# b. Cyalakamanol and Natabaria Avid.

In another experiment orthobords acid was partially dehydrated before esterification with cyclohemenol. A mixture of 15.5 g. (0.25 mole) of orthobords acid and 100 ml. of dry toluons was heated under rollum using a constant water separator. At the end of 2 hours the amount of water removed remained constant at 1.5 ml. (calculated for  $E_0BO_0 \longrightarrow E_0O_0$ , 1.5 ml. of water). Cyclohemenol (25.0 g., 0.25 mole) was added to the flask and the mixture reflected for 2 hours. At the end of this time all the white solid remaining from the first





reflux (presumbly metaboric acid,  $\mathrm{HCO}_2$ ) was dissolved and the total amount of water removed remained constant at 9.0 ml. (thus, h.5 ml. for the second reflux). The theoretical amount of water for 3  $\mathrm{G}_{\mathrm{H},10}\mathrm{H}+3$   $\mathrm{HEO}_3$   $\longrightarrow$   $(\mathrm{G}_{\mathrm{H},10}\mathrm{HO})_2+3$   $\mathrm{Hg}0$  is h.5 ml. Again tolume was distilled off and the resulting white solid filtered and dried at  $100^\circ$  C. under vacuo. Analysis of the solid product (m.p.  $16\mu-167^\circ$  C) gave 8.52% B and a molecular weight of 370 (theoretical for  $(\mathrm{G}_{\mathrm{H},10}\mathrm{HO})_{23}$  8.62% B, molecular weight of 378).

### e. Cyclohemanol and boron trioxide.

The esterification of boron trioxide with cycloheranol in a 1:2 mole ratio was carried out as in the previous experiment (cycloheranol plus orthoboric acid) with boron trioxide substituted for estheboric acid. A mixture of 25.0 g. (0.25 mole) of cycloheranol, 7.5 g. (0.125 mole) of boron trioxide, and 100 ml. of dry toluene yielded 2.2 ml. of water (theoretical for 6  $C_0H_{11}CH + 3 B_0O_3 \longrightarrow 2$  ( $C_0H_{11}CHO_3 + 3 H_2O_3$ ), 2.25 ml. of water). Analysis of the white solid product (m.p.,  $16l_1-167^\circ$ C.) gave 8.71% B and a molecular weight of 368 (theoretical for  $(C_0H_{11}OHO)_3$ ) 8.62% B, molecular weight of 378).

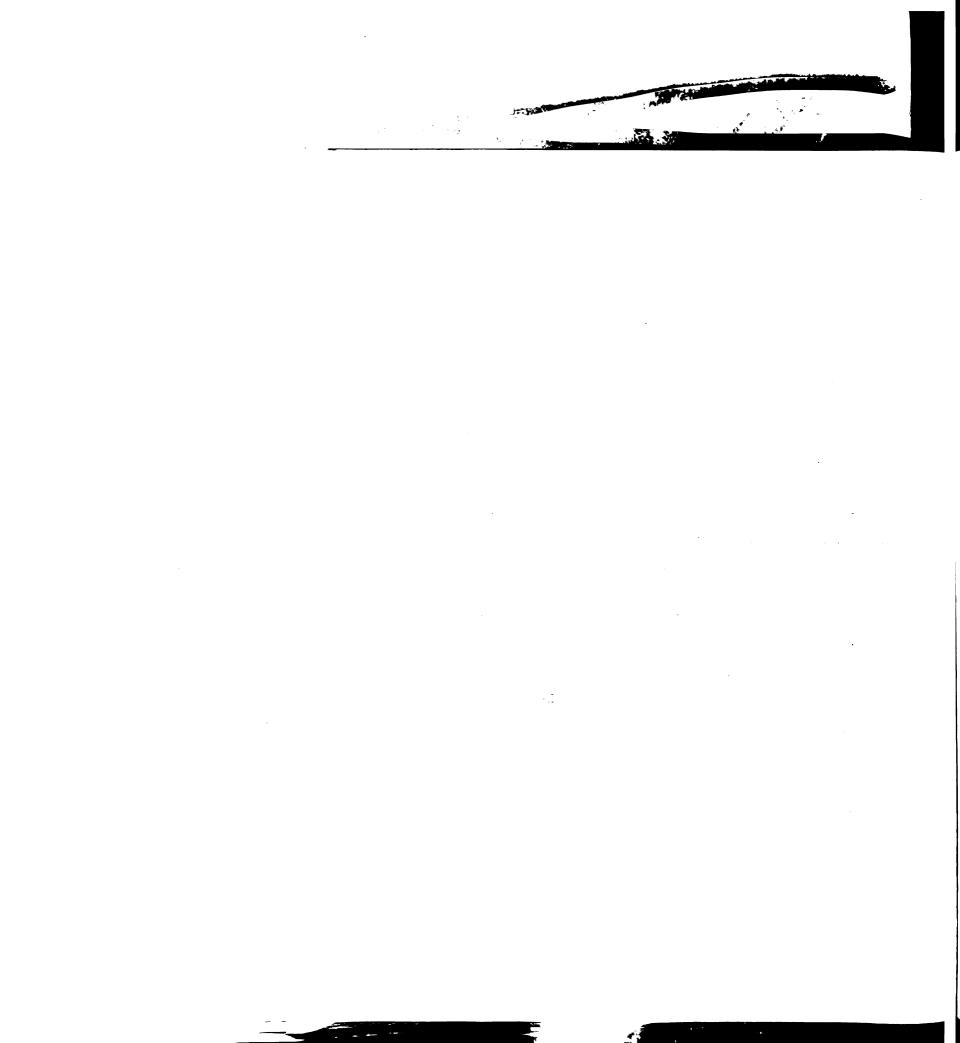
## Basetian of Cycloheranol and Tricycloheranyboracine in Toluene

To determine if tricyclohexceyborone could be propored by reacting cyclohexcenol and tricyclohexceyboronches in stoichiometric ancusts according to the equation

15.0 g. (0.150 mole) eyelekammal was aided to 9.5 g. (0.025 mole) tricyelchamaphoracine dissolved in 200 al. of dry tolmens. The mixture was refluxed using a constant unter separator with stirring. After 3 hours the amount of unter removed remained at 1.3 ml. (theoretical, 1.35 ml.). Stirring was stopped and the clear solution allowed to cool to room temperature; the solution remained clear. The majority of the tolmens was removed by distribution and the final was cooled to room temperature. A loss-salting white solid resulted. The material was distributed at reduced possessure, the bulk of the material being collected at 195-195 (15 min. The yield of (0.5120)) was 21 g. (913). The white solid (n.p., 55-57° C.) was enalyzed for borons found, 3.585 B; calculated for (0.5120), 3. 3.515 B.

## Discussion said by reducing is burning.

Officement and Here (2) mention the allowybords acid, HER(H)<sub>B</sub>, as a possible intermediate in the properation of the metaborate ester, (HORO)<sub>B</sub>, by enterification of orthoboric acid with 1-mention or cyclohemmal. If the allowybords acid is an intermediate, the reaction would proceed as follows:

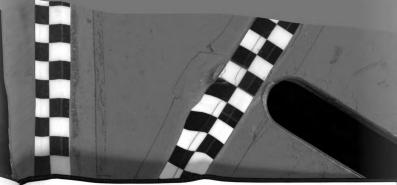


Duty resultion in deligible by detartification of the catalogie and with

In an unsuccessful attempt to prepare the allowyboric acid (by stopping at step 1), 0° Commor and Hace (23) used beamens as the inert solvent. Those investigators stated that "beamens use used in place of tellmens became boric acid does not lose unter below 100°, and thus it might be possible to stop the reaction at the allowy acid stage." However, it use found in this thesis investigation (see Section III, page 60) that orthoboric acid is dehydrated to metaboric acid by refluxing in beamens.

Since metaboric acid is known to be trimeric (70), another possible mechanism is suggested from this thesis study for the reaction of cyclohemmal with orthoboric acid to form tricyclohemosyboracies. The first step would be the dehydration of the orthoboric acid to form metaboric acids

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This reaction is followed by esterification of the metaboric acid with the cyclohesemel:

Exidence in support of this mechanism is 1) the fact that orthoboric acid is dehydrated to netaboric acid by reflucing in telement or beament,

2) metaboric acid is trinscript ((3), 3) metaboric acid reacts with cyclohomomyteric acid has never been isolated.

In the case of the reaction of cyclohoranol with boron triaxide to
form triayclohoranyboranine, a possible mechanism is that the boron
triaxide is partially hydrated to nateboxic acid by initial estacification,
and the notaboxic acid thus formed is then estacified to form the
boronine.

The possibility of the reaction proceeding through the allowyboric acid steps is not discounted by this writer. The reaction most likely proceeds through a combination of possible mechanisms.

The successful preparation of the boracine by reacting triayelehexaryborane, (RO)<sub>3</sub>B, with orthoboxic acid and netshoric acid, together with the negative reaction of the triayelehexaryborane with boron triaxide, indicates that the mechanism of this reaction must proceed through the removal of water. The method of Goubean and Haller (16) (boron trianide plus triallyoxyborene, (10)<sub>2</sub>8) was used to prepare tristhany-, tri-n-propagy-,
tri-n-butoxy-, triisobutoxy-, tri-sec-butoxy-, tri-n-pentoxy-,
tri-n-octoxy-, and tri-n-dodecoxyboroxine. Except for tri-n-dodecoxyboroxine which melted at 10° G., the compounds prepared were liquide at
room temperature. Of the boroxines studied, all decomposed upon
attempted distillation to split off the corresponding trialkoxyborome.
The densities of the boroxines studied increased with increased solecular
weight. The densities followed the relationship D = a + bt over the
temperature range studied. Helecular weight determinations and boron
analyses showed the compounds to have the trimeric formula (2020)<sub>3</sub>.

Addition of an other solution of an emiline (emiline p-chlorosmiline, p-amissidine, p-mitrosmiline, p-aminobemois acid, p-toluidine, and p-aminoscotophenone) to an excess of trimsthaptoroxine in other solution at room temperature produced a precipitate which can be represented by Structure I.



The method of Grubeau and faller (13) both trianted plus trially articles of (12) at a med to proper trianted on the property

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Addition of an ether schedule of an antitue (subline p-ablacessiline)
p-addition, p-admonaline, p-admonale octo, p-schinting, and
p-admonatcherometers) to an account of behalthoughness in ablast school of a contact of a subject school of president and a subject of a school of president of the school of president of the school of president of the school of the scho

Tristhosphorazine was also successfully used in the reaction, but tri-n-propage, tri-n-butage, tri-sec-butage, triischutage, tri-n-pantage, tri-n-cotage, and tri-n-dodecosphorazine yielded no visible reaction products under identical conditions. The products obtained from the reactions of the diamine, bensidine and phenylanediamine, with THS and THS are apparently mixtures containing both three and four dialkosphorazinyl, groups attached to one molecule of diamine.

Our-like polymers are produced from entities and trimethoxyborozine
if the mole ratio of the reactants is near unity and if the reaction
advance is refluced for several hours. Polymers are also obtained in
the absence of a solvent. The repeating unit in the polymer appears
to have the structure II.

Noteboric acid, 1802, was prepared by removal of unter from orthoboric acid, 18802, by assotropic drying with tolume or beasens. When sylene was used to assotrope the unter, the product had a boron content between noteboric acid and boron trioxide. Experimental evidence that Telephonetra was also more appearably used in the reaching but telephone and extended and telephone and telephonetra and the chartes, buretime and phonetra and four telephonetra and telephonetr

obligation of the extinction and boothers one manufor obligate and debtorer of 12 has when the extension of 12 has when it is an abstract the obligation of the control of the extension of the e

Scheberts sold, 1802, was proposed by remised of meter from ordinabords sold, 1,20, by escotiveis drying with follows or beness. Then sylars was med to escotivee the union, the product had a boren emband between unbeloade and have tetaphies. Experienced a vidence that the metaboric acid produced in both the benzene and toluene experiments is MBO\_HII is the multing point (175° C.) and the density (1.76).

X-ray poster diagrams and d values are given for orthoboric acid, metaboric acid, horon tricoide, and the xylene debydration product of orthoboric acid. A comparison of the solubilities of orthoboric acid, metaboric acid, and boron tricoide in a series of aliphatic electeds (methyl-, ethyl-, n-propyl-, n-butyl-, n-myl-, and n-neptyle) is given.

Tricyclohexceyboroxine was propared by reactings 1) gyolohoxanol with orthoboric acid, 2) cyclohoxanol with metaboric acid, 3) cyclohoxanol with boron tricxide, h) tricyclohoxoxyborone with netaboric acid. All of the above reactions were run in toluene with acotropic removal of water. The reaction of cyclohoxanol (6 moles) and tricyclohoxoxyboronine (1 moles) in toluene in stoichiometric assumts yielded tricyclohoxoxyborone as indicated by the following reactions

The attempted preparation of tricyclohexcayborenine by addition of bown tricycle to tricyclohexcayborene dissolved in toluene was unsuccessful.

On enter win and previous in both the beauty (175° 0.) and the density (1.78).

Is constituted in military point (175° 0.) and the density (1.78).

Increp positive diagrams and a values and given for orthinocale acidi, and a second the explanation and the explanation product of metabolish solds. A comparison of the explanation of arthonocale acidi.

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the ablanced proposition of triophiciasagebarmies by addition of boron tectorist to enterpolatearaphorous dissolved in bolume was undoccessful.

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#### FUTURE REPEREMENTAL PROBLEMS

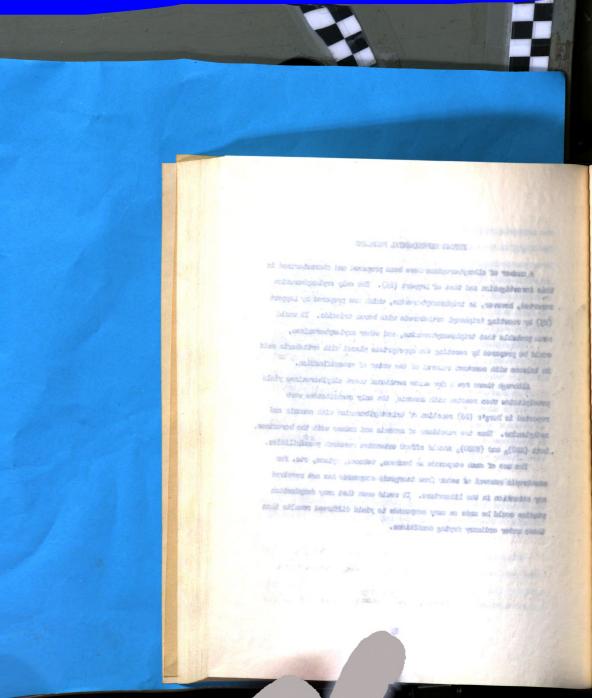
A number of ellosyboroxines have been prepared and characterized in this investigation and that of Lappart (25). The only anylocyboroxine reported, however, is triphenoxyboroxine, which was prepared by Lappart (25) by reacting triphenoxyboroxine, which was prepared by Lappart evaluation of the saylocyboroxine, could be prepared by reacting the appropriate phenol with orthoboric acid in tolurne with constant removal of the unter of esterification.

Although there are a few cases mentioned where ellydboroximes yield precipitates when reacted with amonia, the only quantitative work reported is Burg's (26) reaction of trimsthylboroxime with amonia and methylamine. Thus the reactions of amonia and amines with the boroximes, both (880)<sub>3</sub> and (8880)<sub>3</sub> should afford extensive research possibilities.

The use of such compounds as bemsons, tolurane, sylene, etc. for assotropic removal of sater from inorganic compounds has not received any ettention in the literature. It would seem that many dehydration studies could be made on many compounds to yield different results than those under ordinary drying conditions.

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Fig. 1. and Fig. 1. and index. I., i. many, c. align Con. Sil. 10

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