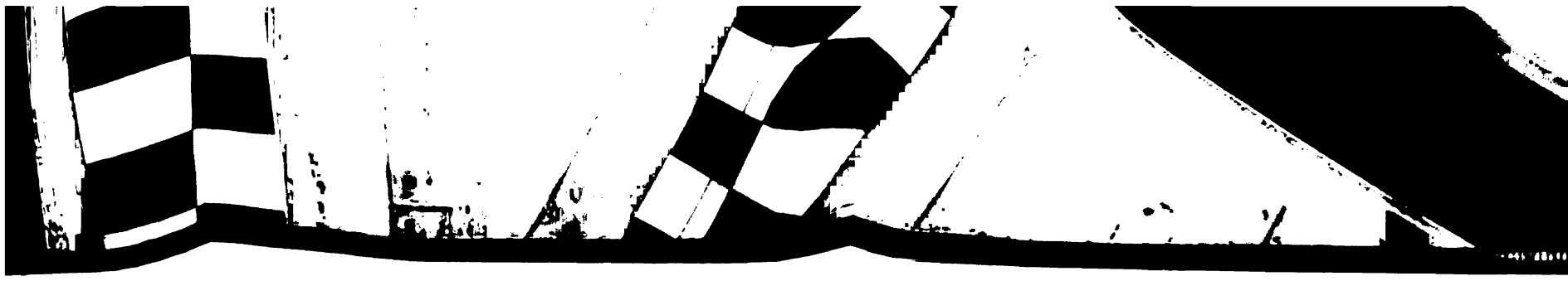


MICHIGAN STATE UNIVERSITY
OF AGRICULTURE AND APPLIED SCIENCE

EAST LANSING, MICHIGAN

PREPARATION AND PROPERTIES OF SOME BOROXINES

By

Lawrence George Kallander

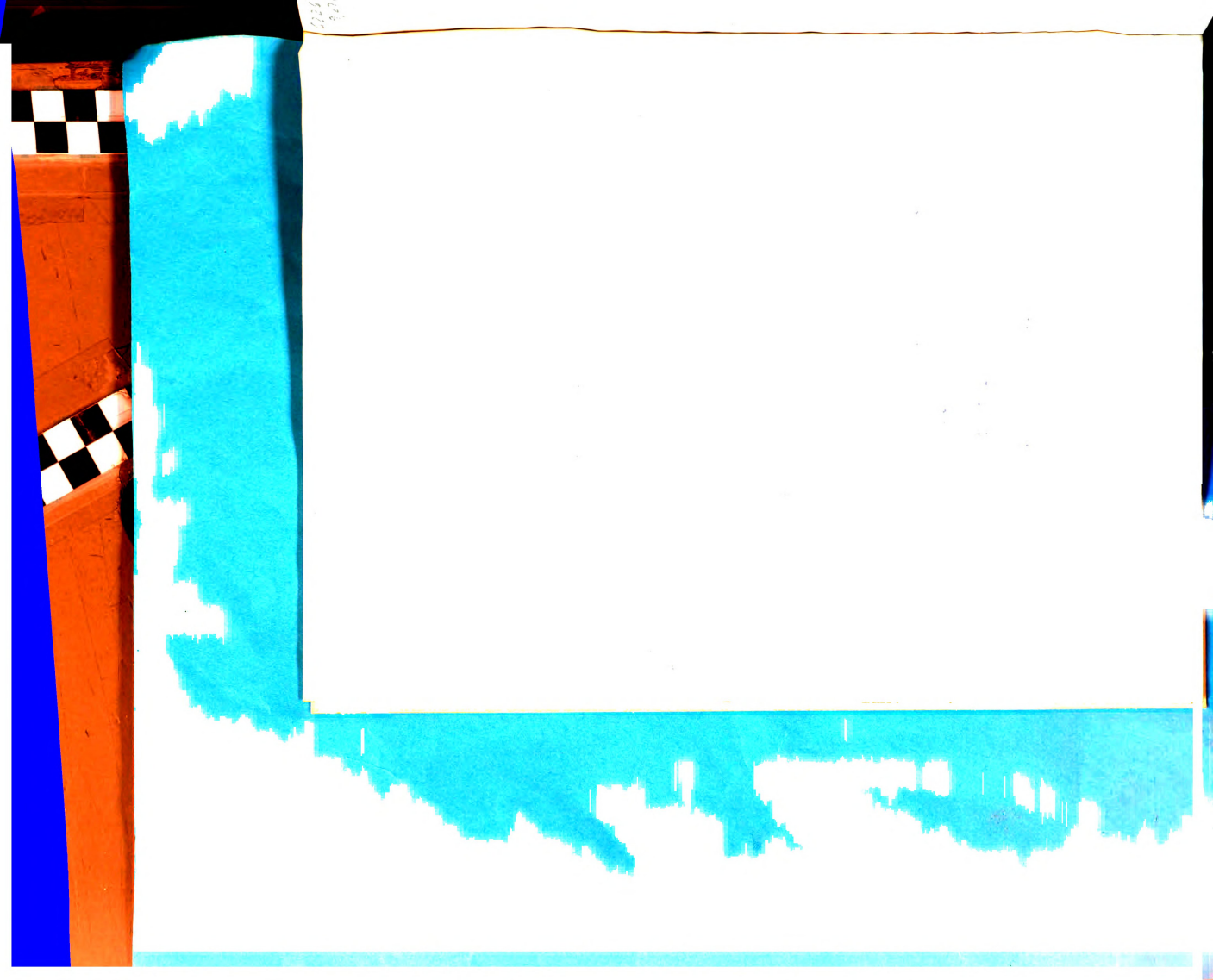
A THESIS

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

DOCTOR OF PHILOSOPHY

Department of Chemistry

1959



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

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PREPARATION AND PROPERTIES OF SOME BOROXOLES

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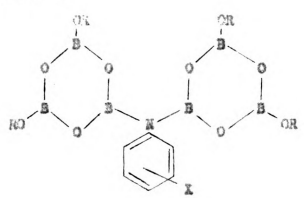
ABSTRACT

A number of trialkoxyboroxines were prepared by reacting boron trioxide with the corresponding trialkoxyborane. The boroxines prepared were triethoxy-, tri-n-propoxy-, tri-n-butoxy-, tri-sec-butoxy-triisobutoxy-, tri-n-pentoxy-, tri-n-octoxy-, and tri-n-dodecoxyboroxine. Except for tri-n-dodecoxyboroxine which melted at 39° C., the compounds were liquids at room temperature. Of the boroxines studied, all decomposed upon attempted distillation to split off the corresponding trialkoxyborane. The densities of the boroxines were obtained. Molecular weight determinations and boron analyses showed the compounds to have the trimeric formula $(ROBO)_3$.

Addition of an ether solution of an aniline (aniline, p-chloroaniline, p-anisidine, p-nitroaniline, p-aminobenzoic acid, p-toluidine, and p-aminoacetophenone) to an excess of trimethoxyboroxine in ether solution at room temperature produced a precipitate which can be represented by Structure I:



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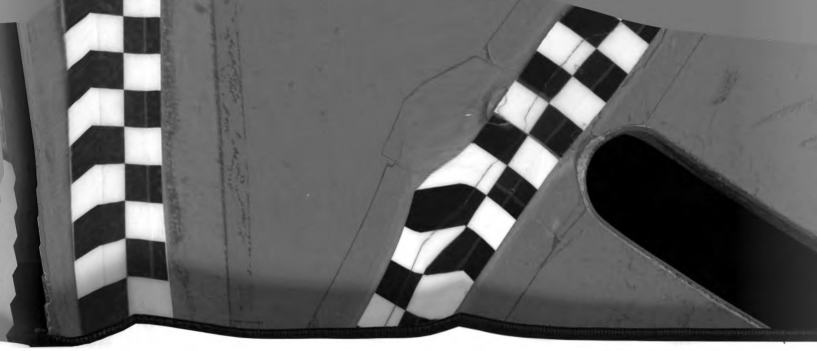


Triethoxyboroxine was also successfully used in the reaction, but tri-n-propoxy-, tri-n-butoxy-, tri-sec-butoxy-, triisobutoxy-, tri-n-pentoxy-, tri-n-octoxy-, and tri-n-dodecoxyboroxine yielded no visible reaction products under identical conditions. The products obtained from the reactions of the diamines, benzidine and phenylenediamine, with tri-methoxyboroxine and triethoxyboroxine are apparently mixtures containing both three and four dialkoxyboroxinyl groups attached to one molecule of the diamine.

Gum-like polymers are produced from aniline and trimethoxyboroxine 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.

Metaboric acid, HBO_2, was prepared by removal of water from orthoboric acid, H_3BO_3, by azeotropic drying with toluene or benzene. When xylene was used to azeotrope the water, the product had a boron content between metaboric acid and boron trioxide. Experimental evidence indicated that the metaboric acid produced in both the benzene and toluene experiments is HBO_2 III. X-ray powder diagrams are given for orthoboric acid, metaboric acid, boron trioxide, and the xylene dehydration product of orthoboric acid. A comparison of the solubilities of orthoboric acid, metaboric acid, and boron trioxide in a series of aliphatic alcohols is given.

Tricyclohexoxyboroxine was prepared by the following reactions: (1) cyclohexanol plus orthoboric acid, (2) cyclohexanol plus metaboric

acid, (3) cyclohexanol plus boron trioxide, (4) tricyclohexoxyborane with orthoboric acid, and (5) tricyclohexoxyborane with metaboric acid. The reaction of cyclohexanol and tricyclohexoxyboroxine yielded tricyclohexoxyborane. The attempted preparation of tricyclohexoxyboroxine by addition of boron trioxide to tricyclohexoxyborane was unsuccessful. All of the above reactions were run with azeotropic removal of water by refluxing the mixtures in toluene.

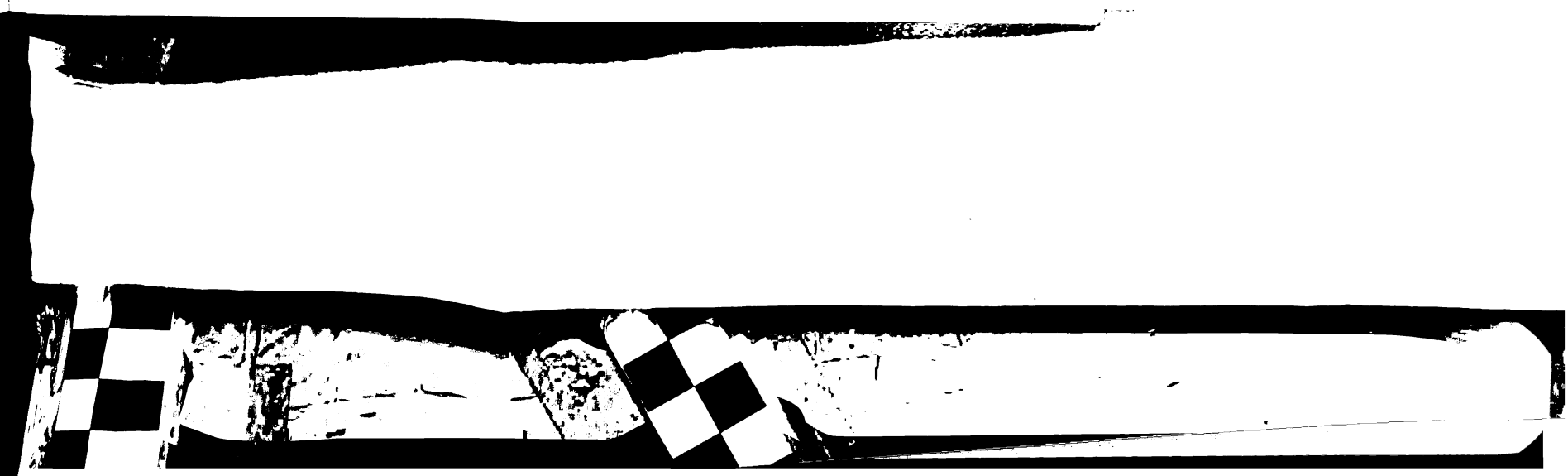


TABLE OF CONTENTS

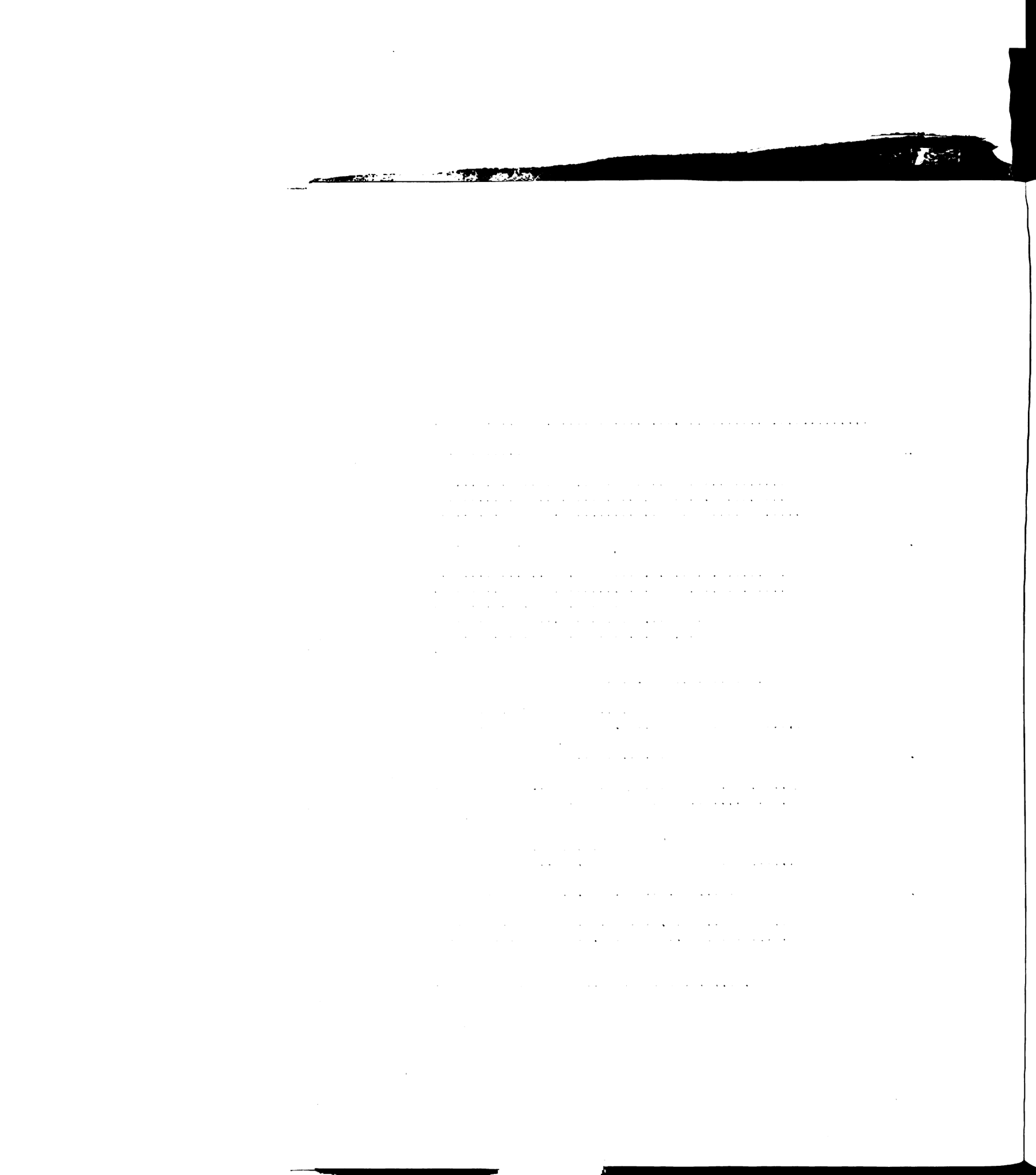


TABLE OF CONTENTS - Continued

LIST OF TABLES

LIST OF TABLES - Continued

TABLE

HISTORICAL

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

I. Preparation and Properties of Some Alkoxyboroxines

II. Reaction of Aromatic Amines with Alkoxyboroxines

III. Dehydration of Orthoboric Acid

IV. Tricyclohexoxyboroxine

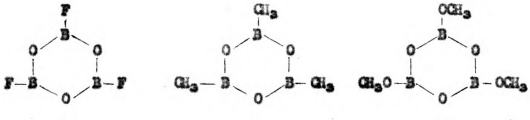
Each of these four sections is divided into three topics: Introduction, Experimental, and Discussion. These four sections are followed by a Summary of the entire thesis study. Lastly, there is a discussion of Future Experimental Problems.

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 on 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 chemistry is exemplified by Lappert's extensive review on organic compounds of boron (4).

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. Haring, and R. K. Birchmistel. 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 trimethoxy- 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.

A survey of the literature of boron-oxygen compounds reveals a variety of nomenclatures for the six-membered ring systems of alternate boron and oxygen atoms. Boric acid anhydrides, boronic anhydrides, boroxines, boroxoles, metaborenilides, metaborates, metaborate trimers, metaboric acid esters, metaboracetates, organoboron oxides, trialkyl triborines, trioxanes, and triboron oxyhalides have been used by various investigators to describe the above-mentioned compounds. The term "boroxole" was ascribed to these compounds by Wiberg (8,9) in analogy to the borazoles, the six-membered ring compounds containing alternate boron and nitrogen atoms. More 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 available positions for substitution in the boroxine ring are designated by numbering in a clockwise direction, beginning with oxygen.

Thus, by the system of Schaeffer and Martig, $(BOF)_3$(I), $(CH_3BO)_3$(II), and $(CH_3OBO)_3$(III) would be



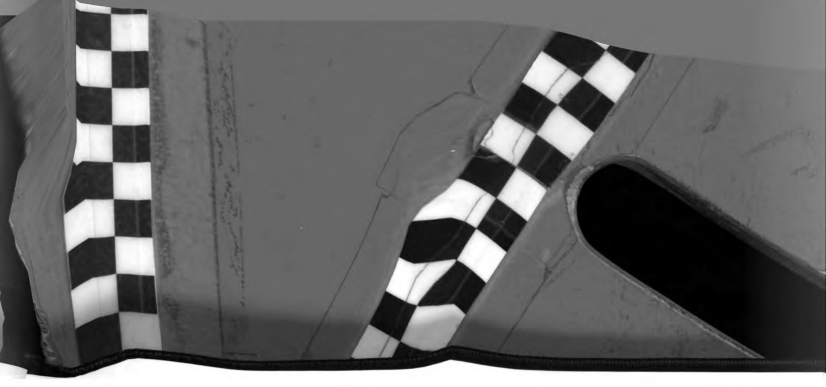
I II III

named 2,4,6-trifluoroboroxine; 2,4,6-trimethylboroxine; and 2,4,6-trimethoxyboroxine, 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 $(RBO)_3$, where R is an organic radical, this type will be reviewed first. These compounds are often called metaborates, since they are esters of metaboric acid HOBO, and have a formula similar to the inorganic metaborates, e.g., $(NaBO_2)_3$ and $(KBO_2)_3$ (10,11).

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

$$B_2O_3 + (RO)_3B \longrightarrow 3ROBO$$



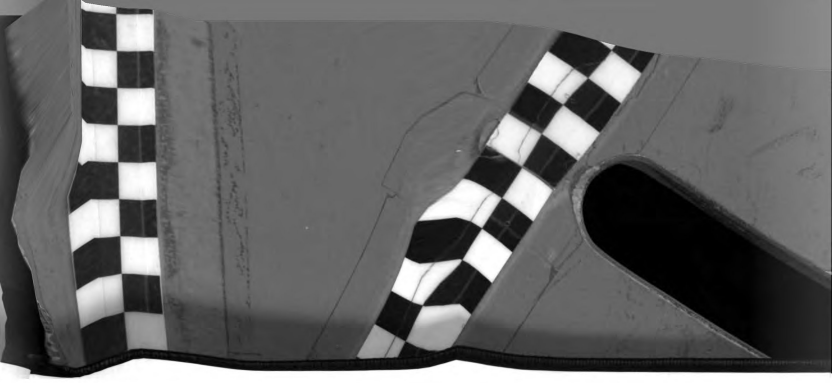
Ethyl metaborate was also obtained by Schiff from ethanol and boron trioxide as follows:

$$C_2H_5OH + B_2O_3 \longrightarrow HOBO + C_2H_5OBO$$

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

Methyl metaborate, $(CH_3OBO)_x$, was presumed by Schlesinger and coworkers (14) to be present as the gummy 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 Etridge and Sugden (15) when an excess of boric anhydride was used in the reaction with methyl alcohol and ethyl alcohol in the preparation of the corresponding orthoborates.

The first study of the properties of trimethoxyboroxole was carried on by Goubeau and Keller (16), who prepared the compounds by a modification of the procedure of Schiff (13), using boron trioxide and the trimethyl ester of boric acid. These investigators found trimethoxyboroxole to be trimeric (cryoscopic and ebullioscopic in benzene). The compound froze at approximately -10° and decomposed above 170° into the starting materials. Raman spectra of trimethoxyboroxole has been reported by Goubeau and Keller (17) to give proof for a six-membered B_3O_3 ring. Ogle (7) prepared trimethoxyboroxine by the method of Goubeau

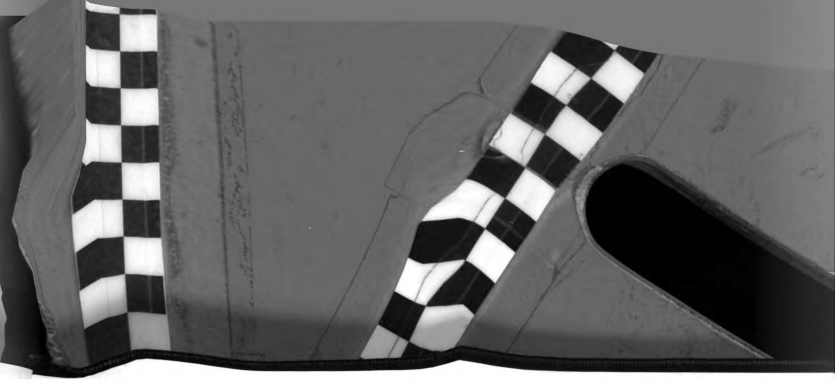


and Keller (16), confirmed the trimeric nature (cryoscopic) in benzene, and obtained the infrared spectrum, the density, and the vapor pressure. From the vapor pressure data, Ogle calculated the boiling point, the heat of vaporization, and Trouton's constant for trimethoxyboroxine.

The above-mentioned data conflicts with a recent study by Carpenter, Hughes, and Bergman (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 Raman 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 molecular weight, boiling point, freezing point, viscosity, refractive index, density, dielectric constant, and conductivity. Examination of these data showed a continuously varying composition rather than a solution of $(CH_3OBO)_3$ in the excess component.

Povlock (19) reacted trimethoxyboroxine with arylgrignards in the preparation of arylboronous acids. The yields were much greater than those obtained by earlier methods.

Metaboroacetate, BO_2Ac, is mentioned by Dimroth (20) as the product when acetic anhydride is split off by heating pyroboroacetate, B_2OAc_4, at 150-60°. Crystallization from acetic anhydride regenerates pyroboroacetate.



The melting point for isopropylmetaborate ester is listed as 47-59° by United States Borax and Chemical Corporation (21).

Tri-n-butoxyboroxine was prepared by Ogle (7) by reacting diboron trioxide with tri-n-butoxyborane. Ogle showed by molecular weight determination (cryoscopic in benzene) that this compound 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 Corporation (21).

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

$$(n\text{-BuBO})_3 + 1\tfrac{1}{2}\ O_2 \longrightarrow 3\ BuOBO$$

the product being the n-butyl ester of metaboric acid. The n-butyl metaborate thus prepared was reported to be monomeric (cryoscopic in benzene).

O'Connor and Hass (23) attempted to prepare n-butyl metaborate acid by esterification of boric acid with an equimolar quantity of n-butanol and azeotropic 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)

attempted to prepare tri-t-butyl borate by the azeotrope method, using t-butanol, boric acid, and benzene.

When O'Connor and Nace (23) heated equimolar quantities of l-menthol or cyclohexanol and boric acid under reflux in toluene two molar equivalents of water were formed and the respective metaborates were obtained in practically quantitative yields.

$$3ROH + 3H_3BO_3 \longrightarrow (ROBO)_3 + 6H_2O$$

Molecular weight determinations showed the compounds to be trimers. Pyrolysis at 270° of l-menthyl metaborate trimer (m.p. 113-15°) and cyclohexyl metaborate trimer (m.p. 165-67°) yielded menthene and cyclohexene respectively. L-Menthyl metaborate trimer was found to hydrolyze to l-menthoxyboric acid, $ROB(OH)_2$, in moist air.

In this present thesis study, a number of trialkoxyboroxines (trimethoxy-, triethoxy, tri-n-propoxy-, tri-n-butoxy-, tri-sec-butoxy-, tri-iso-butoxy-, tri-n-pentoxy-, tri-n-octoxy-, and tri-n-dodecoxyboroxine) were prepared by reacting boric anhydride and the corresponding alkyl orthoborate. Since the completion of this author's experimental work, Lappert (25) has published an article on the preparation of methyl-, ethyl-, n-propyl-, isopropyl-, n-butyl-, isobutyl-, and sec-butyl metaborate by decomposition of the corresponding dialkylchloroboronate either under reflux for a stated time or by adding a catalyst. The above mentioned alkyl metaborates 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

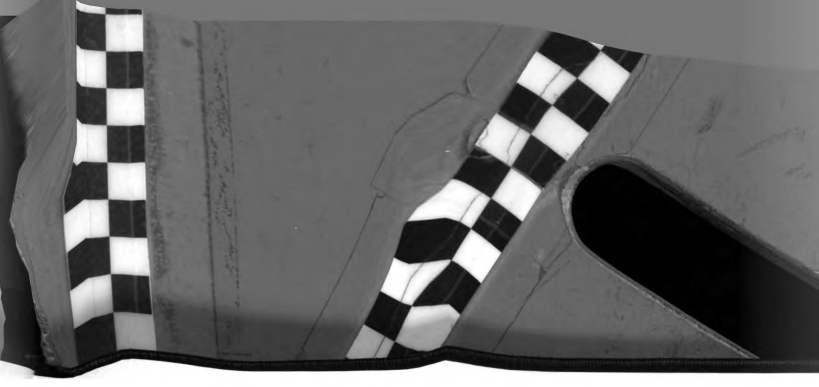
$$\mathrm{Mn(I)} + \mathrm{Ti^{IV}Cl^{-}} \longrightarrow (\mathrm{MnO})^{2} + \mathrm{Cl^{0}_{2}}$$

In Isoelectronic Quantitative Layers.

Although at room temperature one obtained or diphenoxy was part, only re-, rather is polymo-mole ester-, pyrido only was pyrene.

Upon O-Ozone wu Iso (I2) higher colorate diuretics of I-oxalyl I-phenyl, pyrido only was pyrene.

applied to hydro tri-o-poly pyrene in the reaction vessel, nuts

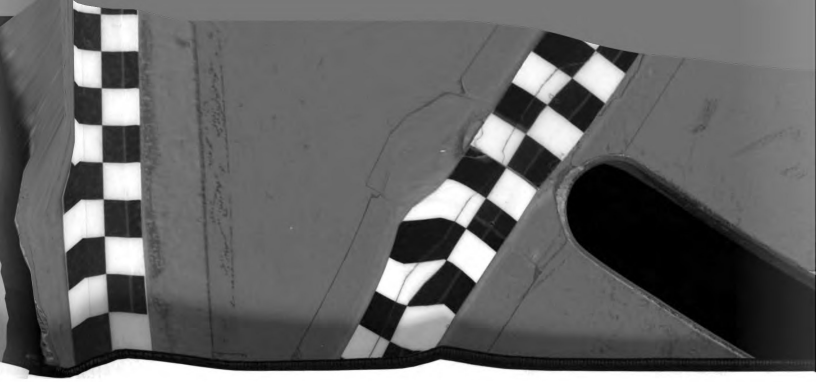


affected by dissolving the product in a large volume of an inert anhydrous solvent, filtering, and evaporating the filtrate under reduced pressure. The infrared spectra and indices of refraction of the metaborates were obtained by Lappert (25) who also reported that attempted distillation of the metaborates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

The largest group of boroxines is the one in which the R in $(RBO)_3$ is an alkyl or aryl group. These compounds are often called boronic anhydrides, since they are usually prepared by the dehydration of a boronic acid, $RB(OH)_2$. The reaction

$$3RB(OH)_2 = (RBO)_3 + 3H_2O$$

has been carried out both by thermal means and by the use of dehydrating agents. The alkyl and aryl boroxines are more numerous in the literature than the alkoxy and aryloxy boroxines. This is probably due to the fact that unlike the latter, the former may be purified by distillation without decomposition and the parent boronic acids are available. The fact that the compounds $RB(OH)_2$, from which the anhydrides $(RBO)_3$ are prepared, are common, whereas there is only one case of a compound $ROB(OH)_2$ being reported (23), becomes more interesting if one views the "parent" compounds, HOBO and HBO. Metaboric acid, HOBO, is well-known (1 mole orthoboric acid, H_3BO_3, minus 1 mole H_2O equals 1 mole metaboric acid, HOBO). However, the "parent" compound "HBO" has never been isolated. Attempts by Burg (26) to prepare this acid by reacting



trimethyl boroxole with diborane, B_2H_6 or boroxole, $H_3B_3H_6$, were not successful. Ogle (7) studied the reaction of trimethoxyboroxine with sodium hydride, but did not obtain the desired HBO.

Leppert (4), in an extensive review of organic compounds of boron, lists a table of physical constants of boronic anhydrides 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. Thus a more thorough description of the preparation, identification, and properties of the alkyl and aryl 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 organoboric acids. An examination by these investigators of the data demonstrated that the organoboric acids studied do not associate in nitrobenzene 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 Salt Lake City and that the products have high molecular weights. Derivatives of boric acid studied were:

Phenyl-
p-Tolyl-
m-Chlorophenyl-
p-Chlorophenyl-
p-Bromophenyl-
o-Phenetyl-
p-Phenoxyphenyl-
α-Naphthyl-

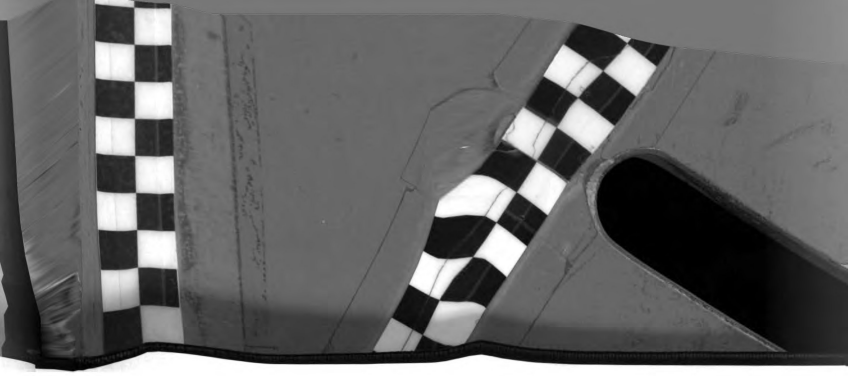
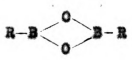


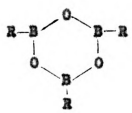
TABLE 1

PHYSICAL CONSTANTS OF BORONIC ANHYDRIDES

R in $(RBO)_3$	Melting Point (°C.)	Boiling Point (°C.)	References
CH_3-	-38	79	16,17,26,30,31,32
n-C_2H_5-			33
n-C_3H_7-			34
n-C_4H_9-		138/18 mm.	22,28,29,33,35,36,37,38,39,42
i-C_4H_9-			34
t-C_4H_9-		66-68/5 mm.	40,41
n-C_5H_{11}-			37,38
i-C_5H_{11}-			34
n-C_6H_{13}-		149/5 mm.	29
C_6H_{11}-			38
C_6H_5-	214-216		27,28,34,41,42,43,44,47
o-$CH_3C_6H_4$-	160-161		45,47
m-$CH_3C_6H_4$-	160-161.5		47
p-$CH_3C_6H_4$-	259-260		27,28,47,49
$C_6H_5CH_2$-	140		51
o-ClC_6H_4-	167-169		50
m-ClC_6H_4-	178-179		27,28,47
p-ClC_6H_4-	211-262.5		27,28,47
p-BrC_6H_4-	301-302		27,28,47,48,49
p-$CH_3OC_6H_4$-	204-207		47
m-$CH_3OC_6H_4$-	159		49
m-$C_2H_5OC_6H_4$-	152-153		50
p-$C_2H_5OC_6H_4$-	171		50
o-$C_2H_5OC_6H_4$-			27
o-$O_2HC_6H_4$-	280-281		52,53
m-$O_2HC_6H_4$-	285-286		47,53
m-$C_2H_5OOCC_6H_4$-	136-138		47
p-$C_2H_5OOCC_6H_4$-	198-200		47
o-$C_2H_5OC_6H_4$-	195		51
2,4-$(CH_3)_2C_6H_3$-	202		46
3,4-$(CH_3)_2C_6H_3$-	226		46
2,5-$(CH_3)_2C_6H_3$-	176		46
p-$C_2H_5OC_6H_4$-			27
α-$C_{10}H_7$-	207		27,28,45,49
β-$C_{10}H_7$-	266		45

Kinney and Ponta (28) then made an investigation of the structure of the organoboron oxides. 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 cryoscopically in nitrobenzene. A consideration of the data showed that the organoboron oxides cannot have the simple formula RBO. Kinney and Ponta 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 oxides to that of boron oxide (boric anhydride) in which at least one oxygen bridge (OBOBO) 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 oxygen atoms. This comparison led Kinney and Ponta to suggest the formulas below rather than merely associated molecules

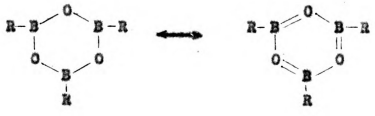




The trimeric formula was adjudged to be similar to those accepted for the trimers of the aldehydes, thioaldehydes, and thioketones. Derivatives of boron oxide studied by Kinney and Ponta were:

Phenyl-
p-Tolyl-
m-Chlorophenyl-
p-Chlorophenyl-
p-Bromophenyl-
α-Naphthyl-

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



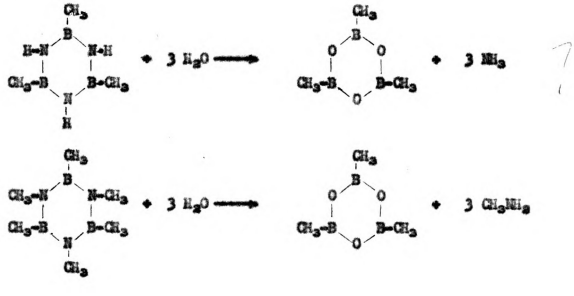
The lowest member of the alkyl boroxines, trimethyl boroxine, has been prepared by various methods. As is the usual case with the first of a homologous series, this boroxine has undergone a more complete study than many of the others.

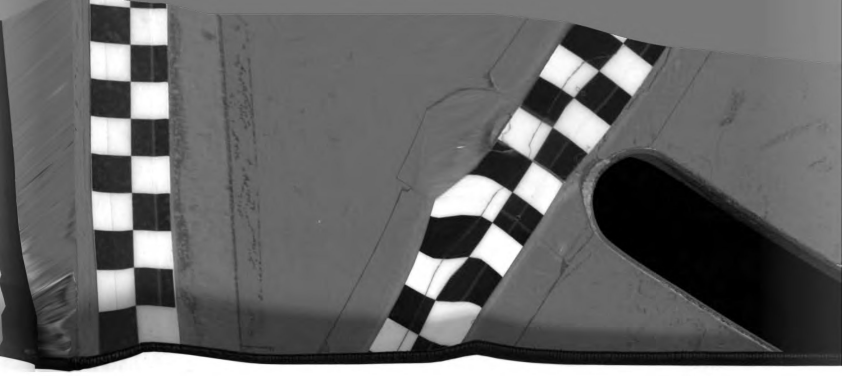
Burg (26) first prepared methylboric anhydride by subliming methylboric acid through anhydrous calcium sulfate in a vacuum system. The molecular weight of the compound, obtained by Burg by vapor pressure measurements, showed the compound to be a trimer, $(CH_3BO)_3$. The heat of

vaporization and Trouton's constant were calculated. The anhydride formed a monotrimethylamine, a mono-ammoniate and a far less-stable diammoniate; 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, CH_3BF_2 in excellent yields.

An electron diffraction investigation of trimethyl triborine trioxone, $(CH_3BO)_3$, by Bauer and Beach (30), lead to the following structure: 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.

Wiberg and co-workers (31,32) prepared trimethyl borazole by partial hydrolysis of β-trimethyl borazole and hexamethyl borazole with three moles of water





The addition of excess water gave methylboric acid and ammonia or methyl amine, respectively.

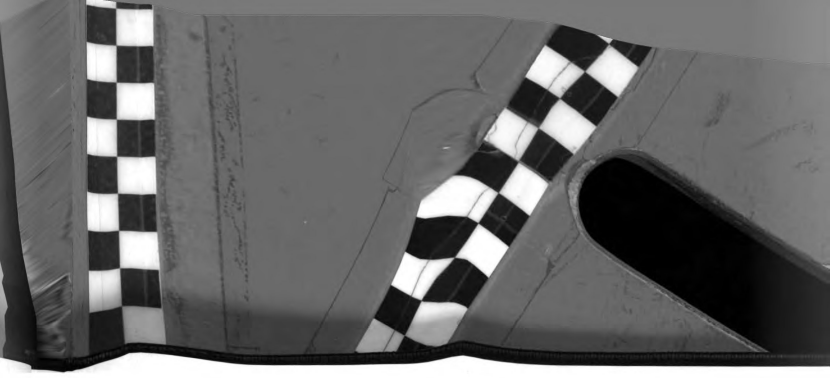
Trimethylboroxole was formed by Goubeau and Keller (16) from the compound, boric oxide, B_2O_3, and trimethyl borines, $B(CH_3)_3$, at 300-330°C. and 15-20 atm. in a 6 hour reaction.

$$B_2O_3 + B(CH_3) = (CH_3BO)_3$$

It formed a water-clear liquid which in humid air hydrolyzed slowly to form nice crystals of methylboric acid. Vapor pressure measurements showed the compound to be a trimer. Raman spectra by Goubeau and Keller (17) confirmed the trimeric nature of the trimethylboroxole.

In a recent study Keller and Perrine (33) reported that ethylboronic acid, $C_2H_5B(OH)_2$, could not be dehydrated to ethylboroxine, $(C_2H_5BO)_3$. The same paper reports the preparation of ethylboroxine by the thermal decomposition of butylboroxine above 700°C.

Krause and Nitsche (34) examined a number of trialkylborines (n-propyl, isobutyl, and isoamyl) and concluded that the normal auto-oxidation (controlled by slow admission of air) gives rise to esters of the aliphatic boronic acids 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 autoxidation of tri-n-butylborine, the formation of the alkylboron oxides, reported by Krause and Nitsche was attributed to hydrolysis of the ester by a limited amount of water (atmospheric



moisture) after the initial oxidation:

$$RB(OR)_2 + H_2O = RB(OH)OR = RBO + ROH$$

Snyder, Kuck, and Johnson (29) prepared n-butylboron oxide (1-butaneboronic anhydride) by heating n-butyl boronic acid under reduced pressure or by warming the acid with thionyl chloride. The trimeric oxide formed was identified by chemical analysis and molecular weight determinations. These investigators found that the oxide reacted with water to regenerate the acid. When anhydrous ammonia was bubbled into a solution of the oxide in dry ether, a white crystalline precipitate was formed. Heat was generated when the oxide was added to phenylhydrazine, aniline, methylaniline, dimethylaniline, diethylamine, triethylamine, di-n-butylamine, and tri-n-butylamine, but a solid was not obtained in any case. Treatment of an ethereal solution of the anhydride at -65° with a considerable excess of n-butylmagnesium bromide 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 (ebullioscopic in benzene).

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

1. $(C_4H_9BO)_3$ (l) + 3 H_2O + Aq ⟶ 3 $C_4H_9B(OH)_2$·Aq

$$H = -11.6 \pm 0.002 \ \frac{\text{Kcal}}{\text{mole}}$$

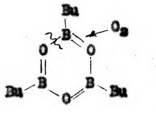
2. $C_4H_9B(OH)_2$ (c) + Aq $\longrightarrow$ $C_4H_9B(OH)_2 \cdot Aq$

$\triangle H = 2.7 \pm 0.001$ $\frac{Kcal}{mole}$

3. $(C_4H_9BO)_3$ (l) + $3H_2O$ $\longrightarrow$ 3 $C_4H_9B(OH)_2$ (c)

$\triangle H = -19.6 \pm 0.04$ $\frac{Kcal}{mole}$

Grummitt (22) found that n-butylboron oxide undergoes quantitative oxidation and depolymerization 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 Grummitt, but could not be confirmed by rate measurements because the kinetics were complex.



$\longrightarrow$ $BuBO(O_2)$ + 2 BuBO

$BuBO(O_2)$ + BuBO = 2 BuOBO

Gluns (37) prepared trimeric n-butyl boron oxide, n-amyl boron oxide, and n-hexyl boron oxide by the method of Snyder, Kuck, and Johnson (29), utilising thionyl chloride to dehydrate the respective alkylboronic acids. For n-butyl boron oxide and n-amyl boron oxide, he determined the infrared spectra and determined the densities and refractive indices. McCusker and Gluns (38) confirmed the stoichiometry of the reaction of boron fluoride with alkyl boron oxides first proposed by Burg and represented by the equation

$$(RBO)_3 + 2\ BF_3 = 3\ RBF_2 + B_2O_3$$

McCusker and Gluns (38) found that the use of a boronic acid, rather than a boronic acid anhydride, as starting material for the preparation of alkyl difluorboranes has the advantage 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 tetrabromide. Aluminum 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 Gluns (38) suggested that the mechanism of the reaction involves as a first step, co-ordinate 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-butylborane $(C_4H_9B(OH)_2)$, and its anhydride, 2,4,6-tri-n-butylboroxine $(C_4H_9BO)_3$ have been reported in a study by Mattraw, Erickson, and Laubengayer (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 dihydroxyborane, boxine, and water is discussed by these authors.

Keller and Perrine (33) found tributylboroxine to be very stable in the absence of oxygen and water, and to show no appreciable decomposition.

They found, however, that tributyl boroxine decomposed above 700° to yield predominantly triethylborazine and ethylene. In the same study, these workers observed that tributylborazine when treated with aluminum chloride, phosphorus pentachloride, or boron trichloride yielded butyldichloroborine, $BuBCl_2$, while the interaction of the compound with trimethylaluminum, methyl aluminum iodide, or methyl magnesium iodide yielded the analagous trialkyl borine, $BuBMe_2$. Keller and Perrine (33) also found that triisobutylborazine when treated with aluminum chloride formed isobutene and boron trichloride instead of the expected isobutyldichloroborine, iso-$BuCl_2$.

t-Butylboron oxide was prepared by Johnson, Van Campen, and Grummitt (40) by treating t-butylboric acid with thionyl chloride, who found it more advantageous to use the oxide than the acid in making solutions of a known quantity of the pure boronic acid.

Krause and Nobbe (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 (42) observed that traces of ferric chloride caused the decomposition of n-butylchloroboronite yielded n-butylboric acid:

$$R\text{-}BCl\text{-}OR = R\text{-}BO + RCl$$

Snyder, Kuck, and Johnson (29) prepared n-hexylboron oxide by placing the crystalline n-hexylboronic acid in a dessicator over concentrated

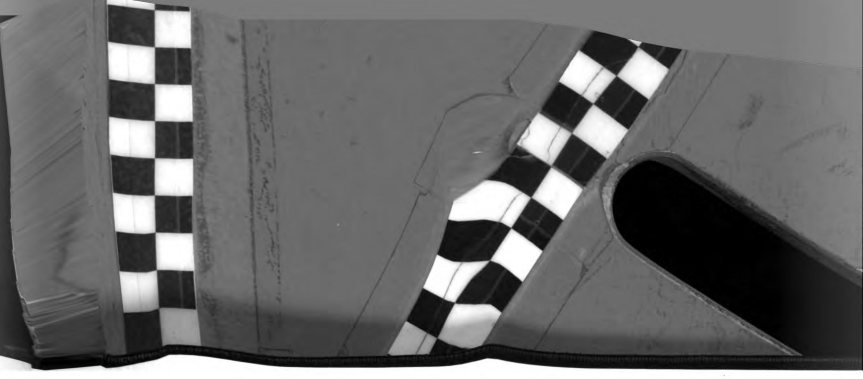
sulfuric acid or phosphorus pentoxide. The liquid anhydride, identified by boron analysis, was also prepared in the same study by refluxing the acid for one hour with an excess (3 moles) of thionyl chloride. On contact with water the oxide regenerated the boronic acid with slight evolution of heat.

References to a large number of aryl boroxines appear in the literature. The first such compound was prepared by Michaelis and Becker (43) who reported that phenylboric acid upon distillation lost water to form phenylboric oxide, C_6H_5BO,

$$C_6H_5B(OH)_2 = C_6H_5BO + H_2O$$

The same workers found that if crystalline phenylboric acid is placed in a dessicator for a long time, it is almost completely converted to phenylboric oxide. Krause and Nitsche (34) confirmed the work of Michaelis and Becker (43) by forming phenylboroxide, C_6H_5BO, by placing phenylboric acid over phosphorus pentoxide in a vacuum. Krause and Nobbe (44) observed that phenylboric oxide and magnesium ethyl bromide reacted vigorously, and that the product when distilled gave boron triethyl, $B(C_2H_5)_3$ and boron tripheryl, $B(C_6H_5)_3$. The molecular weight studies of Kinney and Ponta (26) on phenyl boron oxide have already been mentioned.

Brindley, Gerrard, and Lappert (42) prepared esters of phenylboronic acid by esterification of phenylboronic anhydride with the appropriate alcohol by an azeotrope method.



Able, Dandegaonker, Gerrard and Lappert (44) interacted boron trichloride with phenylboronic anhydride in an inert solvent at -80° to prepare phenyldichlorborane, $PhBCl_2$.

Michaelis and Behrens (45) dehydrated o-tolylboric acid, α-naphthyl boric acid, and β-naphthyl boric acid in a dessicator over sulfuric acid, and identified the resulting oxides by boron analyses. Michaelis (46) also obtained the anhydrides of 2,4-$(CH_3)_2C_6H_3B(OH)_2$, 3,4-$(CH_3)_2C_6H_3B(OH)_2$ and 2,5-$(CH_3)_2C_6H_3B(OH)_2$. Since Kuivila and Hendrickson (47), in a study on the rates of brominolysis of substituted benzeneboronic acids, found that benzeneboronic acid and its anhydride yielded the same specific rate constants, they felt justified in using the acid in some cases (p-BrC_6H_4- and m-$C_2H_5OOCC_6H_4$-) and the anhydride in the following cases:

p-$CH_3OC_6H_4$-
m-$NO_2C_6H_4$-
p-ClC_6H_4-
m-ClC_6H_4-
p-$CH_3C_6H_4$-
m-$CH_3C_6H_4$-
p-$C_2H_5OOCC_6H_4$-

Bean and Johnson (48), 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 Scharrnbeck (49) along with the m-anisyl-, p-tolyl-, and α-naphthyl- derivatives.

Branch, Yabroff, and Bettman (50) reported that if o-chlorophenylboric acid is heated below its melting point (m.p. = 97-98°) the anhydride

picric acid is noted below its melting point (m.p. = 274-276°) the sulphide

Thomas, Thorpe, and Tattersall (20) reported that 2,4-dinitrophenyl-
o-sulphyl- derivatives.

by Kindt and Sonntagbauer (12) along with the o-methyl-, p-ethyl-, and
p-n-propyl- derivatives.

point of the sulphonic. The para sulphonyl, p-carboxyphenyl-, was reported
sensitivities at 313-320 $m\mu$ showed the latter to be the melting
modified with decomposition at 336-43°, recrystallized, and remelted without
phenylthio and upon neutral, reported that p-carboxyphenylthio acid

Bost and Johnson (10), while studying the action of derivatives of

$p\text{-}C_6H_5OCOC_6H_4\text{-}$
$p\text{-}CH_3C_6H_4\text{-}$
$p\text{-}ClC_6H_4\text{-}$
$p\text{-}BrC_6H_4\text{-}$
$p\text{-}IC_6H_4\text{-}$
$p\text{-}CH_3OC_6H_4\text{-}$
$p\text{-}C_2H_5OC_6H_4\text{-}$
$p\text{-}C_6H_5OC_6H_4\text{-}$

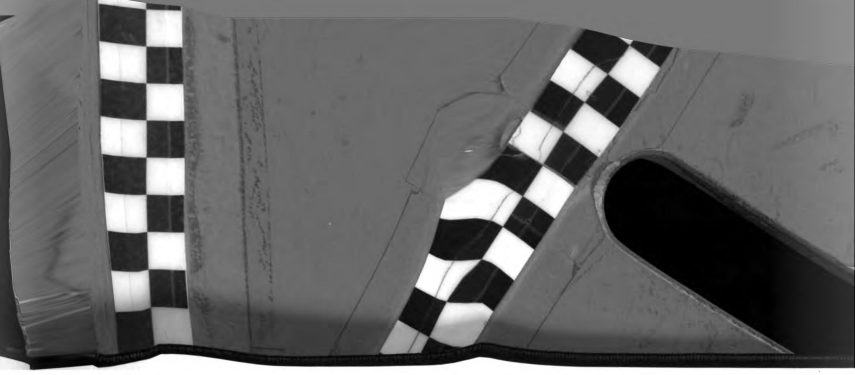
and $m\text{-}O_2NC_6OOC_6H_4\text{-}$) and the sulphate in the following cases

constants. Many fail, possibly in using the acid in some cases ($p\text{-}HOC_6H_4\text{-}$
than benzenesulfonic acid and the sulphonic yielded the very specific type

on the rates of pyrocatechol of substituted benzenesulfonic acids, found
and $2,4\text{-}(O_2N)_2C_6H_3(H)_n$. Bunn Murphy and Hendricks (11), in a study
also effected the sulphonation of $2,4\text{-}(O_2N)_2C_6H_3(H)$, $3,4\text{-}(O_2N)_2C_6H_3(H)$
and identified the resulting esters by Zerewitinoff analyses. Hinsberg (13)
acids, and p-nitrophenyl boric acid in a desulfation over sulfuric acid,

Hinsberg and Bergs (15) designated o-sulfobenzoic acid, o-nitrophenyl
phenone phenylhydrazone, PNBH.

sulfonate with phenylhydrazine sulphite in an ethyl solvent at -80° to
Hein, Dangyanmen, Cerrato and Lagowski (16) investigated boron tri-



slowly forms and the sample does not melt until 167-168°. Some of the acid was dehydrated in a vacuum desiccator containing concentrated sulfuric acid; the anhydride thus obtained (loss of water correct for the ArBO compound) melted at 171-172°. In the same paper, mention is made that m-phenstylboric acid and p-phenstylboric acid melt rapidly with the liberation of moisture and resolidify to form new solids (anhydrides) which melt 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, Yabroff, Branch, and Bettman (51) reported that o-diphenylboric acid forms long needles which melt at 129° with effervescence; after melting resolidification takes place; the new solid (the anhydride) melted at 195°. In the same study, a sample of benzylboric acid upon drying, became warm, gave off white fumes, partially melted, and shrank to an amorphous mass which consisted almost entirely of boric acid. Although other samples did not behave in this manner, Lappert (4), in his review, lists this reference as a preparation of benzylboroxine.

While studying the dissociation constants of organic boric acids, Bettman, Branch, and Yabroff (52) found that o-nitrophenylboric acid melts at 101° (instant immersion) and resolidifies to melt at 145-147°. This melting point corresponds to the value of 143.5-147.7° observed by Seaman and Johnson (53) for the substance obtained by drying o-nitrophenylboric acid in a vacuum desiccator over sulfuric acid. The latter workers

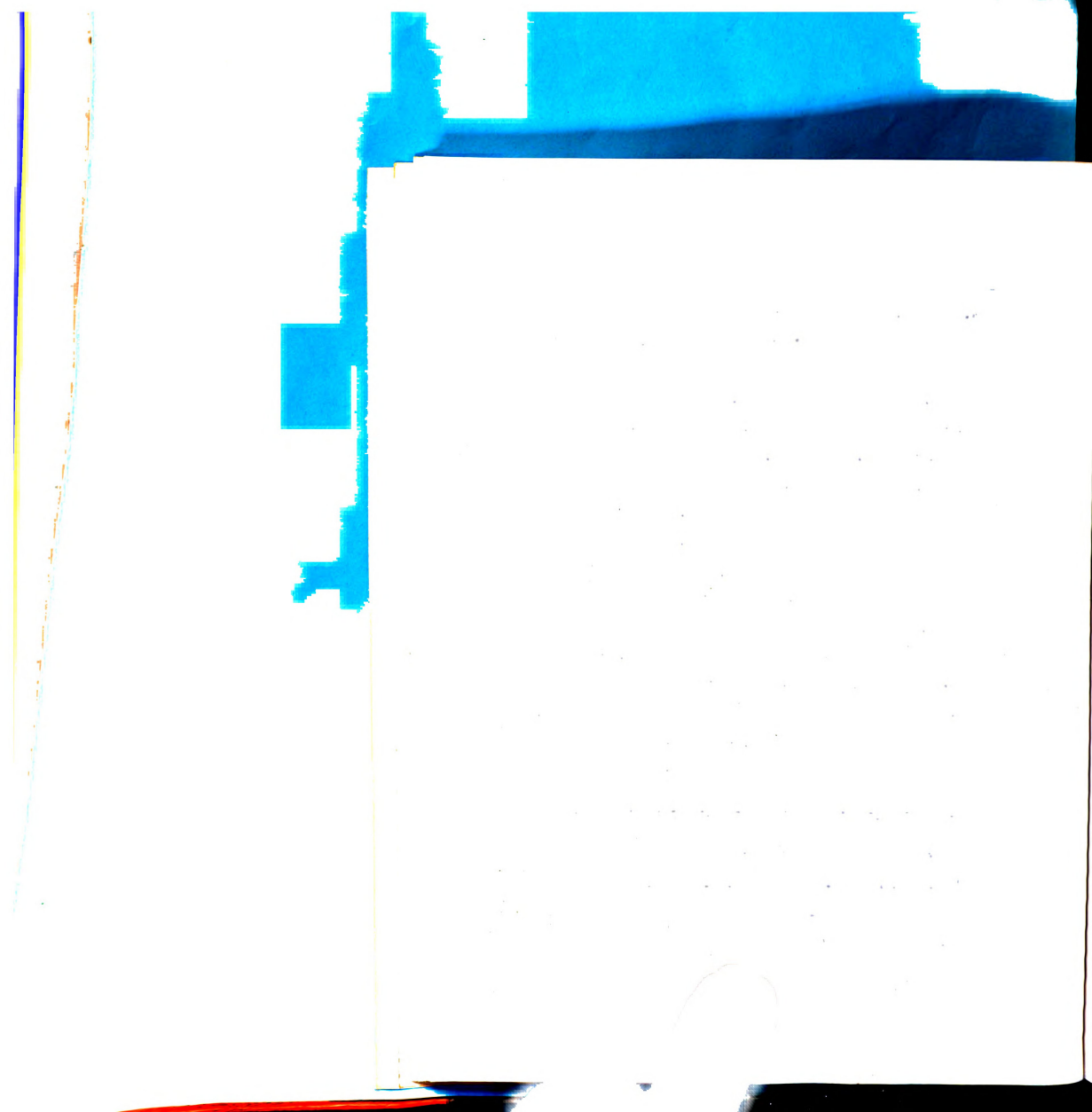
confirmed the formula for the anhydride, $NO_2C_6H_4B = O$, by nitrogen analysis. Seaman and Johnson (53) also found that m-nitrophenylboric acid formed the anhydride when dried to constant weight in a desiccator in vacuo over concentrated sulfuric acid. In the same study, Seaman and Johnson dried m-aminophenylboric acid to constant weight in a vacuum desiccator (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:

$NH_2C_6H_4B(OH)_2$	10.23
$NH_2C_6H_4BO$	11.78
$(NH_2C_6H_4BOH)_2O$	10.95

The nitrogen determinations indicated to the investigators that the completely dried sample was an anhydride 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 anhydride is that the aminoacid may exist as a salt (as do glycine and sulfanilic acid) formed by intramolecular neutralization; thus the elimination of a molecule of water can only occur between two molecules:

$$2\ NH_3^+\text{-}C_6H_4\text{-}BO^-\text{-}OH \xrightarrow{-H_2O} NH_3^+\text{-}C_6H_4\text{-}BO^-\text{-}O\text{-}BO^-\text{-}C_6H_4\text{-}NH_3^+$$

Another class of compounds of the type $(BOX)_3$ is the haloboroxines, in which the X is a halogen. Probably the first indication of such compounds was in studies by Wiberg (54) and co-workers on the reaction of boron trichloride with alcohols and ethers in which dichloroboric



acid esters, BCl_2OR, were formed. 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_2O_3 and BCl_3.

$$BCl_2OR \xrightarrow{50\text{-}70^\circ} RCl + BOCl$$

$$3\ BOCl \longrightarrow B_2O_3 + BCl_3$$

Baumgarten and Bruns (55) proposed a heterocyclic six-ring structure for the reaction product of boron trioxide and boron trifluoride and considered it as a tripolymer of BOF, and not an addition product. The same paper proposed the unstable boron oxyfluoride $(BOF)_3$ for the reaction product of some alkali and alkaline earth salts with boron trifluoride at 450°. Equations for some of the reactions of Baumgarten and Bruns are given as follows:

$$3KBO_2 + 6BF_3 \longrightarrow 3KBF_4 + 2(BOF)_3$$

$$6KNO_3 + 9BF_3 \longrightarrow 6KBF_4 + (BOF)_3 + 3N_2O_5(2NO_2 + K_2O_2)$$

$$3K_2CO_3 + 9BF_3 \longrightarrow 6KBF_4 + (BOF)_3 + 3CO_2$$

$$3Ca(Mg)CO_3 + 3BF_3 \longrightarrow 3Ca(Mg)F_2 + (BOF)_3 + 3CO_2$$

In later work Baumgarten and Bruns (56) studied the reactions of boron trifluoride with aluminum oxide, silicon dioxide, titanium oxide and silicates. The reaction with aluminum oxide occurred at about 450° according to the reaction

$$Al_2O_3 + 2BF_3 \longrightarrow 2AlF_3 + B_2O_3$$

$$Ti^{0}O^{2} + 2Cl^{2} \longrightarrow TiCl^{4} + O^{0}O^{2}$$

according to the reaction

$$2Cr^{0}O^{3} \longrightarrow Cr^{2}O^{3} + 3O^{0}O^{2}$$

and silicon. The reaction with chromium oxide occurred at about 750°C. Boron trifluoride with aluminum oxide, silicon dioxide, titanium oxide and chromium oxide, $BF^{3}O^{3}$ were formed. There was formed in the thermal decomposition of the dichromate acid ester a solid white substance the color which the mixture resumed the formula BOI and which was subsequently decomposed into $B^{2}O^{3}$ and BO^{2}.

$$3\ BOI^{2} \longrightarrow B^{2}O^{3} + BI^{4}$$

$$BI^{4}O^{2} \longrightarrow BI^{2} + BOO^{2}$$

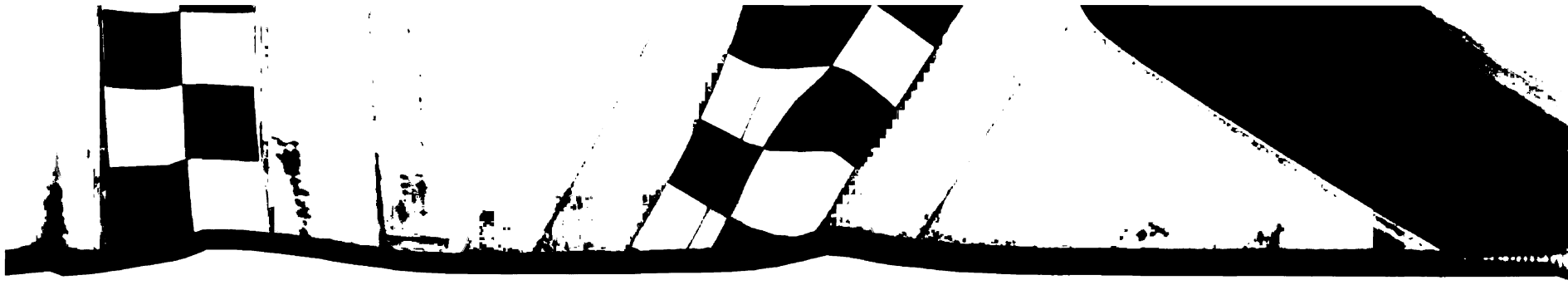
$$2O \rightarrow O^{2}$$

Berzelius and Rose (22) prepared a heteropolyacid ether-ring structure for the reaction product of boron tetrachloride and boron trifluoride and considered it as a derivative of BH^{3} and not an addition product. The same ether produced the unstable boron oxyfluoroacids $(BOH)^{3}$ for the fluoride as $H^{2}O^{2}$. Depending the mode of the reactions of Berzelius reaction product of some glycol and glycerine acids with boron trifluoride and Rose are given as follows:

$$3Ba(NO)O^{2} + 2Br^{3} \longrightarrow 3Br(NO)^{2} + (BOr)^{3} + 3O^{2}$$

$$2Ir^{3}O^{2} + 2Br^{3} \longrightarrow 6BOr^{4} + (BOr)^{3} + 3Ir^{3}O^{3}(BOr)^{3} + K^{3}O^{3})$$

$$6HO^{3} + 6Br^{3} \longrightarrow 3Br^{4} + 3(BOr)^{3}$$



and at this temperature the boron trioxide reacted with boron trifluoride and volatilized, presumably as the oxyfluoride. Other typical reactions in this study were:

$$3SiO_2 + 6BF_3 \longrightarrow 3SiF_4 + 2(BOF)_3$$

$$MSiO_3 + 3BF_3 \longrightarrow MF_2 + SiF_4 + (BOF)_3$$

$$3(Al_2O_3\text{-}2SiO_2) + 21BF_3 \longrightarrow 6AlF_3 + 6SiF_4 + 7(BOF)_3$$

Trifluoroboroxole, trichloroboroxole, and tribromoboroxole were prepared 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 formulas between 250 and 410°. Another paper by Goubeau and Keller (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_3O_3 ring.

Tri-dimethylaminoboroxole, $B_3O_3[N(CH_3)_2]_3$ was formed by Goubeau and Keller (16) from boron trioxide and tri(dimethylamino)borine at 260-300° and 10-15 atmospheres in 3-4 hours. The well-crystallized compounds hydrolyzed easily with water to form boric acid and dimethylamine. The trimeric formula was determined by vapor pressure measurements and also by ebullioscopic measurements in benzene.

$$3(I_2^0P_{3/2}-ICl)^3 + I2Br^0 \longrightarrow (I_2Cl^+ + ICl_2^- + I(ICl)^3$$

$$I2Cl^0 + IBr^0 \longrightarrow IBr^0 + ICl^+ + (ICl)^0$$

$$I2Cl^0 + IBr^0 \longrightarrow I2Cl^+ + Br(ICl)^3$$

in this study were

my volatility, presumably as dye oxidation. Other typical reactions

and at high temperature the boron triiodide reacted with boron trifluoride

Metaborenilide, C_6H_5NHBO, was prepared by Chaudhuri (58) by heating a mixture of boric acid, aniline, and fused zinc chloride at 135-140°.

$$C_6H_5NH_2 + H_3BO_3 \longrightarrow C_6H_5NHBO + 2H_2O$$

In Lappert's review (4) mention is made that "no physical measurements were made, but it seems possible that metaborenilide is trimeric and hence a boranole." Chaudhuri, however, gives data for monomeric C_6H_5NHBO, as determined by the platinichloride method.

A rapid increase in interest of the boroxines for industrial use is evident from recent chemical news items and technical data sheets. Trimethoxyboroxine 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 trimethoxyboroxine may be used in many applications, such as an automotive fuel additive, a test additive for jet fuels, a formulation of self extinguishing fire resistant paints, an ingredient of special fire 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 commercially.

Comerford, Chamberlain, and Shephard (60) found trimethoxyboroxine to be a liquid having unique characteristics which were useful for

to be a liquid having marked dimethylaniline which were useful for

Quantitative. Quantitative, but dropped (2) Trust Schwefelsäure

Impurity", and n-butyl naphthalene column was unreliable commercially.

and a modern detector. It is also significant to note that method

of quick drying material time, a determining agent in chemical reaction,

fine sensitive, a fractionation of time sketching pipeline, a fractionation

of optical fine centrifuge liquid, a procedure of fifteen minutes for

a formulation of cell multiplexer fine measured points, an important

clean, much as an outstanding wind adjusted, a pure solution for pin train,

numerous multiplex and triethylbenzene may be used in many applica-

on a joint fractionation laboratory, and as a fine multiplex fine.

Patterson (2) says the product is not being used in testing special engines,

of the action of power cyclonite or engines using high energy fuels.

Chemistry. Originally requested to make the compound for use in evaluation

testing from recent chemical mono fine and technical data sheets.

A might interest to knowledge of the processes for industrial use is

determined by the plasticizing method.

n pressure.[5] Quantitative. However, given code for monomers $C_6H_5NO_2$, as

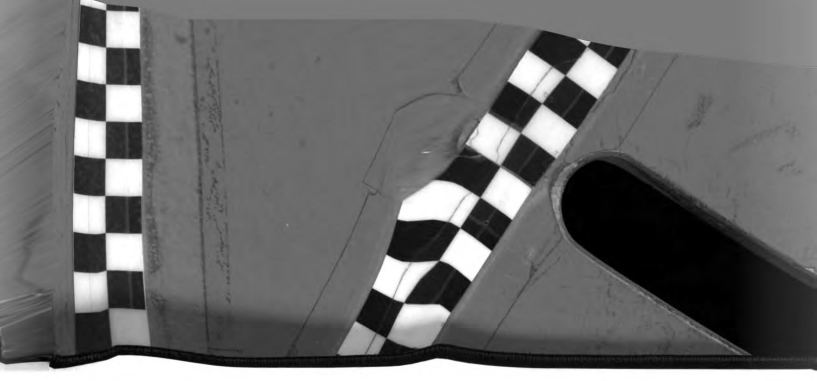
were made, but it seems possible that methoxymethyl is intimate and pecan

In Jaynes's review (3) mention is made that "no physical measurements

$$C_6H_5Br + H_2O \longrightarrow C_6H_5NHO + 2H_2$$

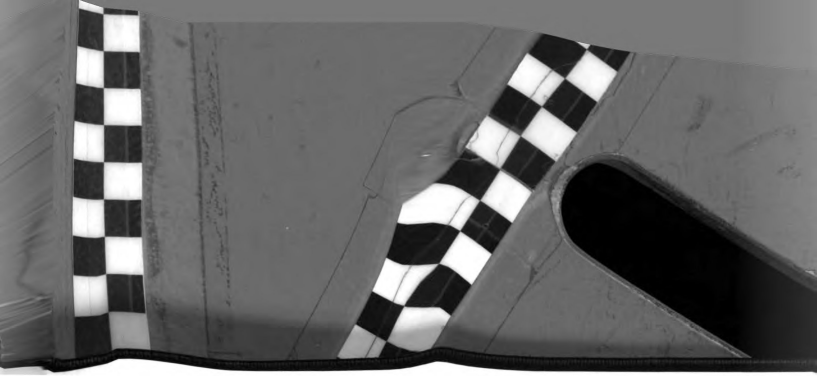
a mixture of boric acid, nothing, and fibre zinc chloride at 212-770°.

Isopropanethio, C_6H_5NO, was prepared by Quantum (28) by heating



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

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 Potash and Chemical state their optimism that the boroxines will find widespread applications in industrial processes in which high boron content compounds in liquid form are desired.



I. PREPARATION AND PROPERTIES OF SOME ALKOXYBOROXINES

Introduction

The first boroxines formed were trimethoxy- and triethoxyboroxine, prepared by Schiff (13) by dissolving boron trioxide or orthoboric acid in the trimethyl and triethyl esters of orthoboric acid, respectively. Goubeau and Keller (16) used a modification of the procedure of Schiff to prepare trimethoxyboroxole, and carried 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 preparation, properties, and structure of trimethoxyboroxine was made by Carpenter, Hughes, and Bergman (18). Since the completion of the experimental work of this thesis study, Lappert (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 alkoxyboroxines previously studied were the trimethoxy- and tri-n-butoxy- compounds. Thus an investigation was undertaken to prepare and study some higher homologues of trimethoxyboroxine.

In this dissertation study, the method of Goubeau and Keller (16) was used to prepare triethoxy-, tri-n-propoxy-, tri-n-butoxy-, triisobutoxy-, tri-sec-butoxy-, tri-n-pentoxy-, tri-n-octoxy-, and tri-n-dodecoxyboroxine. The preparation of triethoxyboroxine is given in detail

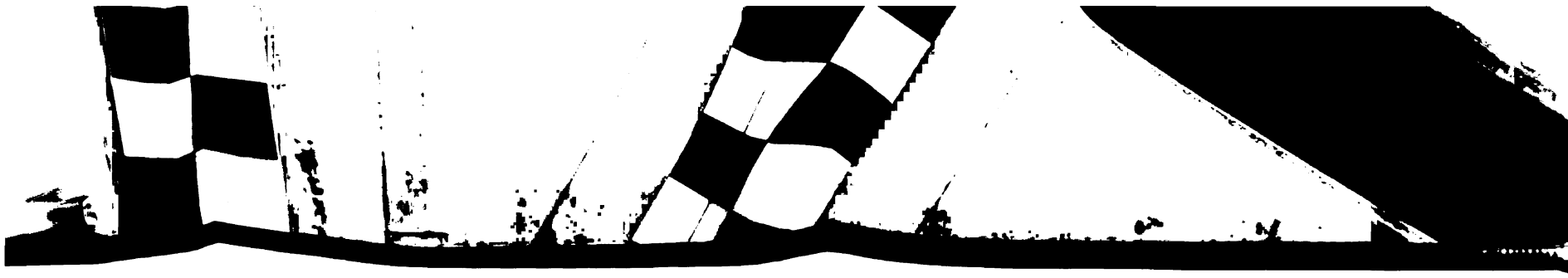
Introduction

The first homologous formal rule 'methane-, ethane-, propane-, butane-, pentane-, hexane-, heptane-, octane-, nonane-, decane-' was introduced by Pouchet (33) by dissolving boron nitride or carbonate into the fluoride and boiling' series of carbonic acid, respectively. Chapman and Muller (34) made a modification of the procedure of Pouchet by replacing tetrahydrofuran' and starting out the first study of the physical properties of the compound. Upon (1) passing air through some impurities' and iso-butyl hydroxide.

In the years of this decade Parkard' however, the only dimethylbutane in-butyl-, isobutyl-, and iso-butyl hydroxide.

Then an investigation was undertaken to isolate and study some higher previously studied were the tetrahydro- and tri-n-butyl- carbonate.

In this dissertation study', the method of Graham and Miller (35) benzene of tetrahydrofuran.

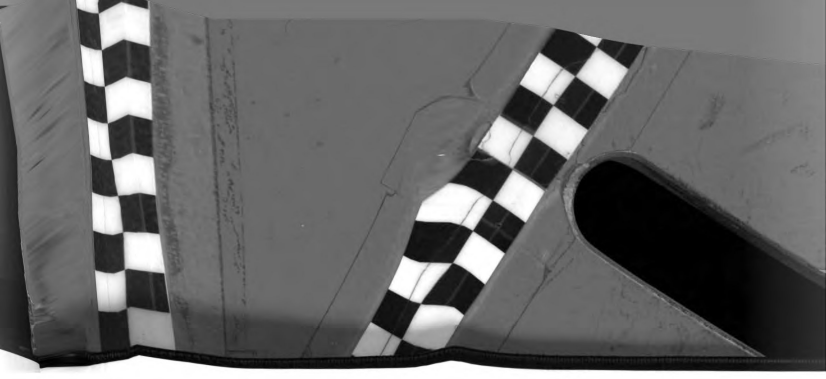


in the Experimental of this Section, the preparation of the other boroxines is summarized. The boiling point and freezing point of each compound was observed, as recorded in Table 2. The density of each compound was observed over a range of temperatures. The boroxines were found to be soluble in a number of organic solvents such as benzene, toluene, diethyl ether, carbon tetrachloride, and chloroform. Molecular weights, determined ebullioscopically or cryoscopically in benzene, showed the compounds to be trimeric. The boroxines hydrolyzed in water to form, presumably, orthoboric acid, and the corresponding alcohol. The addition of ether solutions of a number of aromatic amines to ether solutions of trimethoxy- and triethoxyboroxine yielded precipitates; no visible precipitates were observed when the other boroxines were used.

Experimental

Triethoxyboroxine

To prepare triethoxyboroxine, the two reactants, diboron trioxide (50.0 g., 0.840 moles) and triethoxyborene (122.5 g., 0.840 moles) were heated under reflux in a round-bottom flask at a temperature such that the triethoxyborene would drip slowly back into the flask. The mixture was stirred rapidly by a glass-covered magnetic stirring bar. The top of the reflux condenser 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 flask. The flask was stoppered and placed in a -78° C. bath



of dry ice and isopropyl alcohol for six hours; the liquid froze 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 glass-stoppered bottle.

The colorless, viscous compound hydrolyzed rapidly in water. (In some of the runs the preparations were light-yellow liquids.) The compound was analyzed for boron by dissolving and hydrolyzing it in hot water and titrating the liberated boric acid with standard base, using mannitol, according to the procedure outlined in Kolthoff and Sandell (62). The compound was found to contain 15.3 per cent boron (theoretical percentage for $(C_2H_5OBO)_3$, 15.2). The molecular weight, determined cryoscopically in benzene was found to be 210 (theoretical for $(C_2H_5OBO)_3$, 215).

The triethoxyboroxine froze as a clear glass at approximately -45° C. A flask containing a thermometer well 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 reached 210° 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 gummy residue of boron trioxide. Analysis of the water-clear distillate showed 7.50 per cent boron (theoretical percentage for $(C_2H_5O)_3$ B, 7.41.

The density of the triethoxyboroxine, from 0.0° C. to 80.0° C. was determined by using a one-milliliter dilatometer. The dilatometer was

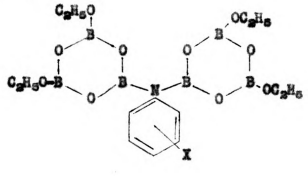
weighed empty and then filled with triethoxyboroxine and reweighed. The volume was obtained by reading the liquid level on the graduated stem to within 0.001 cc. The dilatometer was immersed in a Dewar flask until the liquid level in the dilatometer was covered with water of the desired temperature. 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

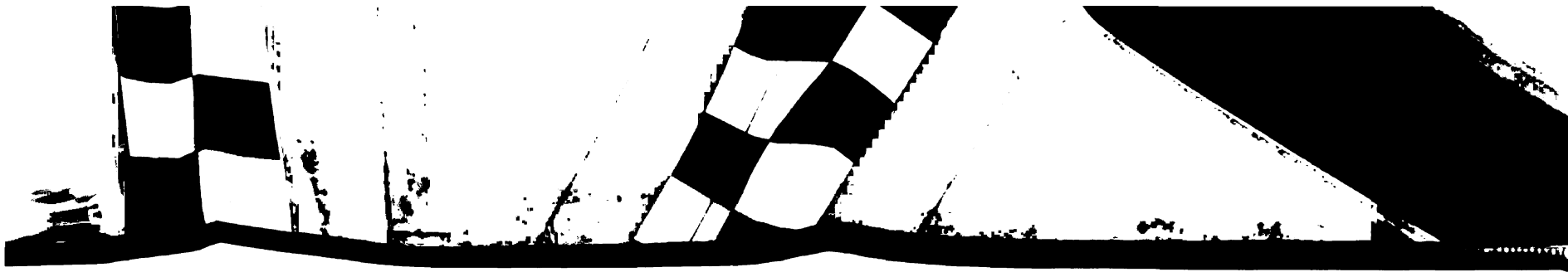
$$D g/cc = 1.113 - 0.0011\ t$$

where t equals degrees centigrade.

The triethoxyboroxine is miscible with benzene, toluene, 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 ether solutions of triethoxyboroxine. Solid compounds to which the following empirical structure has been assigned were obtained:



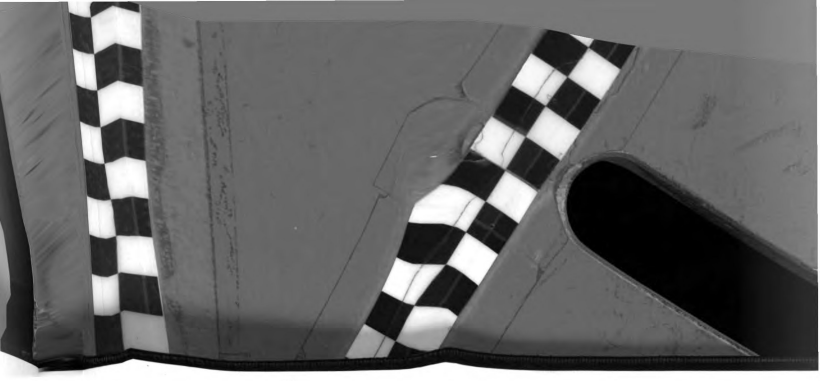


The nature of this reaction is discussed in more detail in Section II, page 46.

Tri-n-propoxy-, tri-n-butoxy-, tri-sec-butoxy-, triisobutoxy-, tri-n-pentoxy-, tri-n-octoxy-, and tri-n-dodecoxyboroxine

The preparation of these alkoxyboroxines followed the procedure detailed for triethoxyboroxine and will only be outlined in this next section. A paddle 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-n-dodecoxyboroxine was a white wax-like solid at room temperature; the other boroxines studied were viscous compounds at room temperature. The tri-n-propoxy-, tri-n-butoxy-, tri-sec-butoxy-, and tri-isobutoxyboroxines were water-clear liquids (although some preparations of the tri-n-propoxyboroxines yielded a light yellow liquid). The tri-n-pentoxy- and tri-n-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 gummy 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 trialkoxyboranes. 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-sec-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 above -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 hydrolyzed in water; the rate of hydrolysis appeared to diminish with increased molecular weight of the compounds, being especially slower for the tri-n-octoxy- and tri-n-dodecoxyboroxines. The formation of an immiscible substance (probably n-dodecyl alcohol) was apparent in the hydrolysis of tri-n-dodecoxyboroxine.

The boroxines were analyzed for boron by dissolving and hydrolyzing them in hot water and titrating the liberated boric acid with standard base, using mannitol, according to the procedure outlined in Kolthoff and Sandell (62). To assure complete hydrolysis in the analyses of the tri-n-octoxy- and tri-n-dodecoxyboroxines, these compounds were dissolved in hot water in iodine 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 4; in all cases the percentage of boron

TABLE 2

MELTING POINTS AND DECOMPOSITION POINTS OF THE BOROXINES AND BOILING POINTS OF THE DISTILLATES

R in $(RBO)_3$	Melting Point of $(RBO)_3$ °C.	Decomposition Point of $(RBO)_3$ °C.	Boiling Point of Distillate °C.
Methyl	10[a]	170[a]	68[a]
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-Amyl	-50	340	240
n-Octyl	-25	275/2 mm.[b]	190/2 mm.
n-Dodecyl	30	310/2 mm.[b]	275/2 mm.

[a] Reference 16.

[b] No distillate at 375° at 1 atm.

TABLE 5

MELTING POINTS AND ISOMERIZATION POINTS OF THE DIPHENYLTINS

R in $(RCH_2)_2Sn(C_6H_5)_2$	Melting Point of $(RCH_2)_2Sn(C_6H_5)_2$	Decomposition Point of $(RCH_2)_2Sn(C_6H_5)_2$	Boiling Point of Diphenyltin
Methyl	70[a]	170[a]	65[a]
Ethyl	-15	220	107-110
n-Propyl	-28	285	171
n-Butyl	-45	295	190
Iso-Butyl	-70	276	204
Cyclo-Butyl	-72	252	183-186
n-Amyl	-80	340	240
n-Octyl	-24	272/2 mm.[b]	198/2 mm.
n-Lauryl	30	317/2 mm.[b]	218/2 mm.

[a] Reference 16.

[b] Tin dialkyltins at 275° at 7 mm.

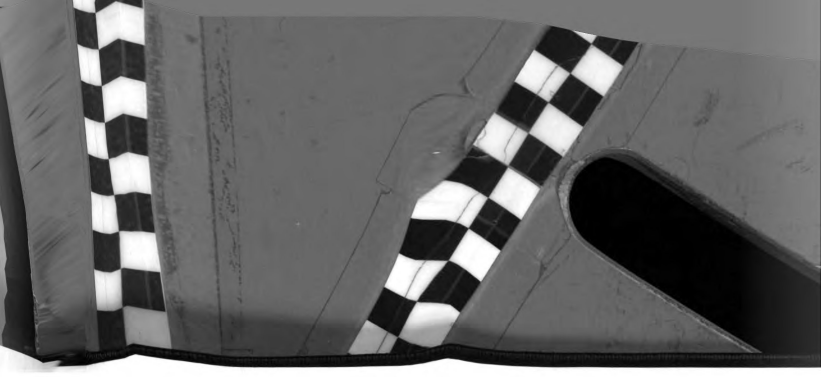


TABLE 3

BORON ANALYSES OF THE DISTILLATES FROM THE BOROXINES

R in $(ROBO)_3$	Per Cent B Found in Distillate	Per Cent B Calculated for $(RO)_3$ 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-Amyl	4.05	3.98
n-Octyl	2.65	2.71
n-Dodecyl	2.02	1.91

TABLE 3

BOILING TEMPERATURE OF THE ISOMERIC ALKYL ETC BORATINES

B-Tri (Alkyl)$_3$	In Dilute Alkyl	For Unit X Dipole	For Unit X Dipole (90)^2 X
Ethyl	4.20		7.12
n-Propyl	6.83		5.75
n-Butyl	8.00		4.70
Iso-Butyl	6.75		4.70
Sec-Butyl	8.80		4.70
n-Hexyl	8.05		3.98
n-Octyl	5.65		2.73
n-Decanyl	5.05		1.97

TABLE 4

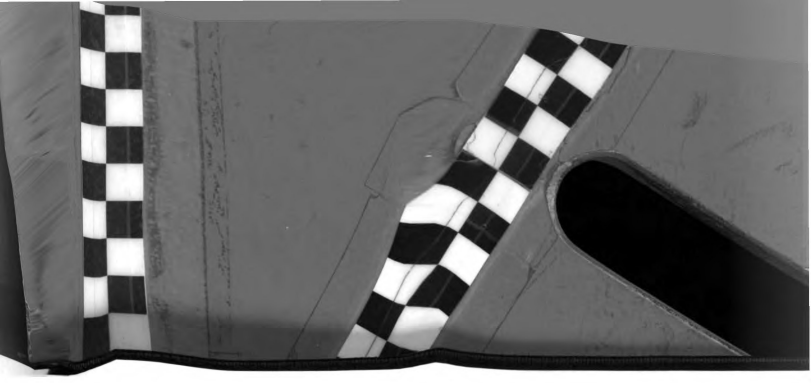
BORON ANALYSES AND MOLECULAR WEIGHTS OF THE BOROXINES

R in $(ROBO)_3$	Per Cent B		Molecular Weight	
	Found	Calculated	Found	Calculated
Ethyl	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	480	467
n-Dodecyl	4.92	5.00	604	625

TABLE I

MOLAR ABSORPTIVITIES AND RETENTION VALUES OF THE PORPHYRINS

π → π* (Soret)	Pyrrole	Unoxidized	Found	Unoxidized
Etio I	12.3	12.3	210	215
meso-Hpty	12.6	12.1	207	207
meso-Hpty	10.8	10.9	290	295
Etio-Hpty	11.0	10.9	292	299
Etio-Hpty	10.8	10.9	305	299
meso-Hpty	9.69	9.52	330	343
meso-Hpty	6.91	7.00	530	467
meso-Hpty	4.95	5.00	640	625



found agreed with the value calculated for the trialkoxyboroxine, $(ROBO)_3$.

The molecular weights of the boroxines were obtained either ebullioscopically or cryoscopically in benzene. The results obtained (Table 4) indicate that the compounds have the trimeric formula, $(ROBO)_3$.

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

$$D = a + bt \quad (t \text{ equals degrees Centigrade})$$

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 benzene, toluene, ethyl ether, acetone, carbon tetrachloride, and chloroform. Two milliliters each of the boroxine and the respective solvent were used in the mixtures. Solution was not as rapid with tri-n-dodecoxyboroxine 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 methylene, dichloride and ethyl ether by evaporation of the solvent.

Unlike the trimethoxy- and triethoxyboroxines, the addition of ether solutions of aniline and ring-substituted anilines to ether

other mixtures of miking and ring-evaporation suffices to obtain
Unlike the trichloro- and tetrachloromethane, the addition of
volatile solvents as methylene dichloride and ethyl ether by evaporation
of the solvent.
The solvent was made by this method to remove the borneline from
the solvent" ira Ingwert (32) recovered the borneline from such mixtures,
borneline, and was eight (assumed) by boiling.
Methanol was not so rapid with tri-and tetrachloromethane as with the other
the impurities and the azeotropic mixture used in the distance.
conditions, such as temperature, and viscosities. The difficulties such of
Table II.
The borneline are checkle with benzene, ethyl ether,
each benzene at 25° C. calculated from 2 = equation, are given in
use calculated for that borneline. These equations, and the density of

$$D = a + bt \quad (2 \text{ equals degrees Centigrade})$$

for each benzene, an equation

Density data are given in Table C-II. From the density data obtained
by the mass dilatometer method as with the tetrachloromethane. The
(mass)^2.
The molecular weights of the benzene were checked either graphic-
mechanically or cryoscopically in benzene. The results obtained (Table I)
indicate that the compounds have the formula formula, ($HCCl_3$)$_2$.
The densities of the benzenes, from 0.0-80.0°C, were determined

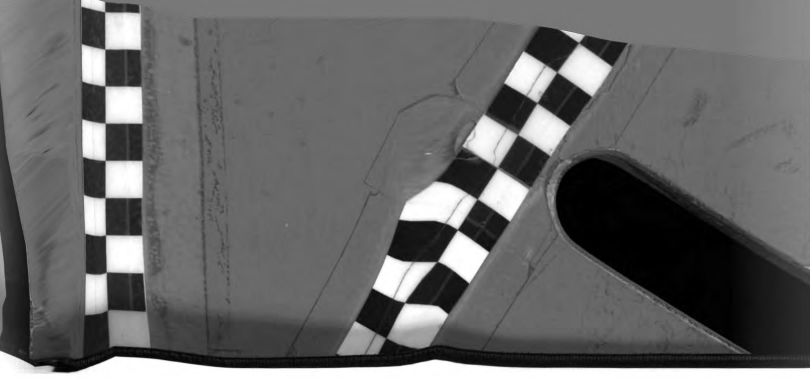


TABLE 5

DENSITY OF TRIETHOXYBOROXINE

Temperature (°C. ± 0.1)	Observed Density (g./c.c., ± 0.001)	Calculated Density* (g./c.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

*$D = 1.113 - 0.0011\ t$

TABLE 5

DENSITY OF ETHANOL/WATER MIXTURE

Temperature (°C ± 0.1)	Observed Density (g/cm³ ± 0.001)	Calculated Density[a] (g/cm³ ± 0.001)
0.0	1.113	1.113
10.0	1.105	1.105
20.0	1.097	1.097
30.0	1.089	1.089
40.0	1.080	1.080
50.0	1.071	1.071
60.0	1.062	1.062
70.0	1.052	1.052
80.0	1.042	1.042
90.0	1.032	1.032

[a] $\rho = 1.113 - 0.0021\ t$

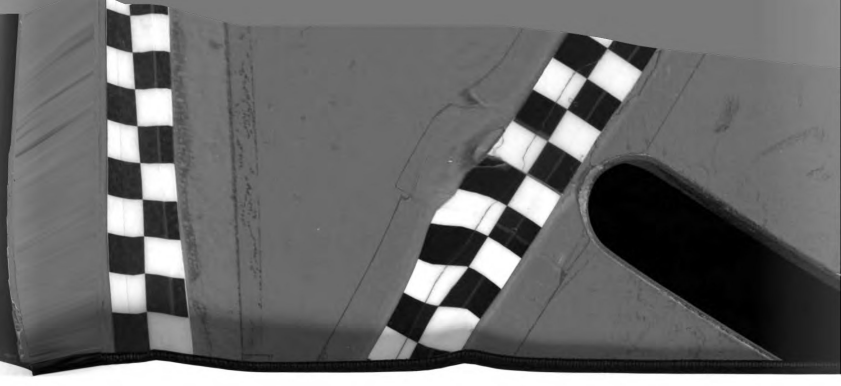


TABLE 6

DENSITY OF TRI-n-PROPOXYBOROXINE

Temperature (°C. ± 0.1)	Observed Density (g./c.c., ± 0.001)	Calculated Density* (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

*$D = 1.047 - 0.0010\ t$

TABLE 6

REFRACTIVE OF VILE-A-VIS/CHLOROFORM SYSTEM

Temperature (°C. ± 0.2)	Observed Refractive Index ($n_D^{t°C.}$ ± 0.0002)	Calculated Refractive Index ($n_D^{t°C.}$ ± 0.0027)*
0.0	1.4647	1.4647
10.0	1.4598	1.4597
20.0	1.4547	1.4547
30.0	1.4497	1.4497
40.0	1.4448	1.4447
50.0	0.9398	0.9397
60.0	0.9348	0.9347
70.0	0.9298	0.9297

*n_D^t = 1.4647 - 0.0050 t

TABLE 7

DENSITY OF TRI-sec-BUTOXYBOROXINE

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	1.081	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

*$D = 1.090 - 0.0009\ t$

TABLE 4

0.0	1.000	1.000
0.05	1.000	1.000
0.10	1.001	1.001
0.15	1.001	1.001
0.20	1.002	1.002
0.25	1.003	1.003
0.30	1.004	1.004
0.35	1.005	1.005
0.40	1.006	1.006
0.45	1.007	1.007
0.50	1.008	1.008

$\beta = 1.010 - 0.0008\ t$

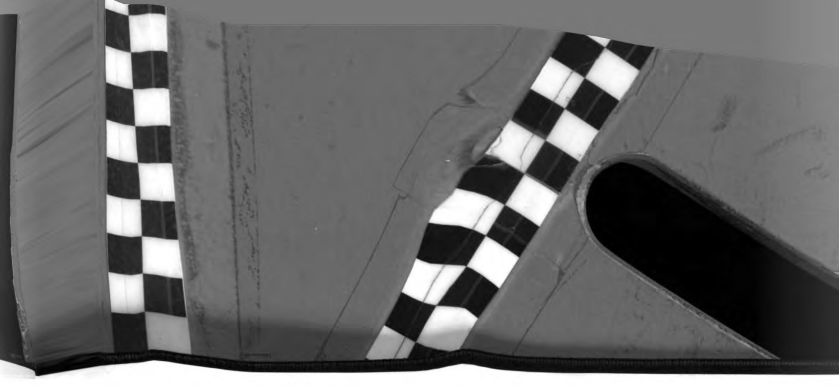


TABLE 8

DENSITY OF TRISOBUTOXYBOROXINE

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

*$D = 1.098 - 0.0010\ t$

جدول ٥

جدول ك الخطوط الطيفية

الموجة (٠٫٠٠ ± ٠٫٠٢)	معامل الانكسار (١٫٥٠٠٠ ± ٠٫٠٠٠٢)	التشتت المولي R_m (٠٫٠٠٠١ ± ٠٫٠٠٠٢)
٠٫٥	١٫٥٣٠	١٫٥٣٠
٤٠٫٥	١٫٥٣٤	١٫٥٣٤
٤٥٫٥	١٫٥٣٨	١٫٥٣٨
٥٠٫٥	١٫٥٤١	١٫٥٤٢
٥٥٫٥	١٫٥٤٥	١٫٥٤٦
٦٠٫٥	١٫٥٤٨	١٫٥٤٩
٦٥٫٥	١٫٥٥٢	١٫٥٥٣
٧٠٫٥	١٫٥٥٥	١٫٥٥٦
٧٥٫٥	١٫٥٥٨	١٫٥٥٩
٨٠٫٥	١٫٥٦٠	١٫٥٦٢

$R_m = ١٫٥٣٠ - ٠٫٠٠٢٥ \, \varepsilon$

TABLE 9

DENSITY OF TRI-n-PENTOXYBOROXINE

Temperature (°C., ± 0.1)	Observed Density (g./c.c., ± 0.001)	Calculated Density* (g./c.c., ± 0.001)
0.0	1.095	1.096
10.0	1.085	1.085
20.0	1.076	1.076
30.0	1.067	1.067
40.0	1.058	1.058
50.0	1.049	1.049
60.0	1.040	1.040
70.0	1.031	1.031
80.0	1.023	1.022

*D = 1.096 - 0.0009 t

TABLE 5.

DENSITY OF ZnI$_2$-CaI$_2$(SATURATED)SOLUTIONS

Temperature (t° ± 0.2)	Observed Density (g_1/cm^3 ± 0.001)	Calculated Density^a (g_1/cm^3 ± 0.003)
0°C	1.985	1.986
10°C	1.975	1.978
20°C	1.965	1.964
30°C	1.951	1.948
40°C	1.938	1.928
50°C	1.910	1.906
60°C	1.890	1.880
70°C	1.873	1.851
80°C	1.853	1.822

$^a d = 1.985 - 0.003\,t$

TABLE 10

DENSITY OF TRI-n-OCTOXYBOROXINE

Temperature (°C., ± 0.1)	Observed Density (g./c.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

*$D = 0.936 - 0.0007\ t$

TABLE II

DENSITY OF DEUTERIUM OXIDE

Temperature (°C. ± 0.2°)	Observed Density (g./c.c. ± 0.003)	Calculated Density* (g./c.c. ± 0.003)
0°	0.934	0.934
10°	0.930	0.929
20°	0.925	0.922
30°	0.918	0.913
40°	0.908	0.902
50°	0.897	0.891
60°	0.884	0.878
70°	0.867	0.864
80°	0.847	0.849
90°	0.827	0.833

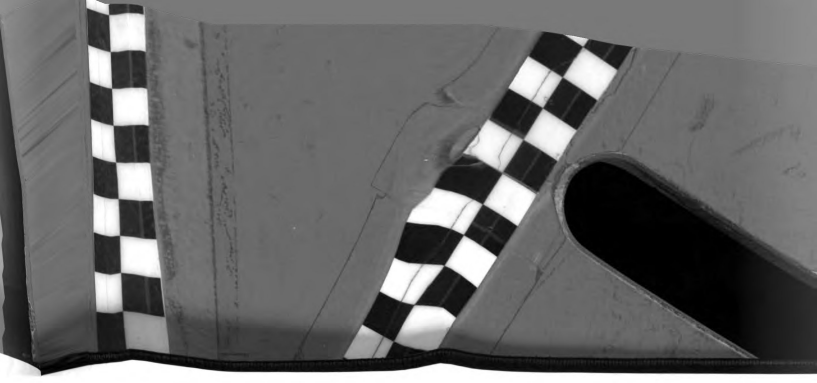
* $D = 0.934 - 0.0014\ t$

TABLE 11

EQUATIONS FOR DENSITIES AND CALCULATED DENSITIES AT 25°C.

R in $(ROBO)_3$	Equation for Density	Density at 25°C. (calculated)
Methyl	$D = 1.242 - 0.0012\ t$[a]	1.212
Ethyl	$D = 1.133 - 0.0011\ t$	1.136
n-Propyl	$D = 1.047 - 0.0010\ t$	1.022
n-Butyl	$D = 1.030 - 0.009\ t$[a]	1.008
iso-Butyl	$D = 1.098 - 0.0010\ t$	1.073
sec-Butyl	$D = 1.090 - 0.0009\ t$	1.078
n-Amyl	$D = 1.096 - 0.0009\ t$	1.074
n-Octyl	$D = 0.936 - 0.0007\ t$	0.919

[a]Reference 7.



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

Discussion

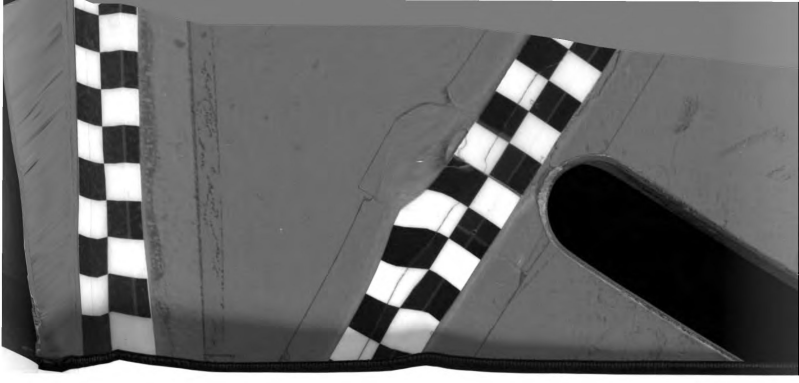
The method of Goubeau and Keller (16) was used to prepare triethoxy-, tri-n-propoxy-, tri-n-butoxy-, triisobutoxy-, tri-sec-butoxy-, tri-n-pentoxy-, tri-n-octoxy- and tri-n-dodecoxyboroxine. Except for tri-n-dodecoxyboroxine which melted at 30° C., the compounds prepared were liquids at room temperature. Of the boroxines studied, all decomposed upon attempted distillation to split off the corresponding trialkoxyborane, $(RO)_3B$. The temperature required for the decomposition was higher than the boiling point of the trialkoxy borane, the difference varying from 102° for the ethyl compound to 35° for the dodecyl compound. Goubeau, in a study on trimethoxyboroxine, and Lappert (25), working with trimethoxy-, triethoxy-, tri-n-propoxy-, triisopropoxy-, tri-n-butoxy-, triisobutoxy-, and tri-sec-butoxyboroxines, similarly found that the boroxines 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 Lappert. Lappert (25) also found that attempted distillation of the boroxine under reduced pressure caused disproportionation to yield the orthoborate and boron trioxide.

The infrared spectra for the boroxines studied were obtained. However, examination of the spectra indicated that the samples had

became partially hydrolyzed so no conclusions were made from the curves. The infrared spectra of some alkoxyboroxines were obtained by Lappert (25) who concluded that absorption near 720 and 735 cm^{-1} is of good diagnostic value for metaboric esters (boroxines).

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, $(RBO)_3$. 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. Lappert (25) concluded from indices of refraction that trimethoxy-, triethoxy-, triisopropoxy-, tri-n-propoxy-, tri-n-butoxy-, triisobutoxy-, and tri-sec-butoxyboroxine were trimeric.

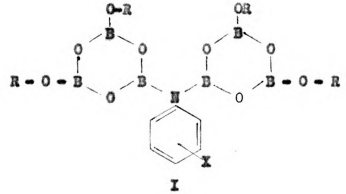


II. REACTION OF AROMATIC AMINES WITH ALKOXYBOROXINES

Introduction

One series of reactions of alkoxyboroxines with amines 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 (4) 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 (trimethoxy-, triethoxy-, tri-n-propoxy-, tri-n-butoxy-, tri-sec-butoxy-, triisobutoxy-, tri-n-pentoxy-, tri-n-octoxy-, and tri-n-dodecoxyboroxine) with the aromatic amines(aniline, p-chloroaniline, p-anisidine, p-aminobenzoic acid, p-nitroaniline, p-aminoacetophenone, p-toluidine, phenylenediamine, and benzidine) was undertaken.

Addition of an ether solution of the aniline to an excess of the boroxine in ether solution at room temperature produced a precipitate which suggested Structure I.



I

Compounds of this type have been prepared from aniline and six substituted anilines and from two aromatic diamines. Tri-methoxy- and triethoxyboroxine have been successfully used as a reagent, but tri-n-propoxy-, tri-n-butoxy-, tri-sec-butoxy-, triisobutoxy-, tri-n-pentoxy-, tri-n-octoxy-, and tri-n-dodecoxyboroxine yield no reaction products under identical conditions. Dioxane and benzene are adequate substitutes for the ether solvent in this reaction; acetone 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 empirical formula is correct has been established by analysis of seven anilines for boron, hydrogen, nitrogen, and chlorine (when present) and analysis of products from reactions of triethoxyboroxine with the same anilines for boron alone. These analyses have also established that the product is a "monomer" rather than a polymer of aniline and the boroxine.
2. That the boroxine is not being decomposed to the alkylorthoborate, which in turn reacts with the aniline, is shown by the fact that aniline does not form a precipitate with the orthoborates. It was also shown that when boron trioxide is added to an ether solution of aniline, no reaction occurs.
3. That the aniline is not altered beyond losing the two hydrogen atoms bonded to the nitrogen is shown by the fact that hydrolysis of the product with hot potassium hydroxide permits quantitative recovery of the aniline.

economy of the suffix.

of the pronoun with the possessive independent pronoun qualifying above pertod to the nickname is shown by the fact that individuals

3. That the suffix is not altered joined into the pleonastic to an other colleagues of suffix, to localize common.

purpose. It was also shown that when pure infinite is added

That that suffixes does not form a coordinate with the suffix

pronoun, rather is form words with the suffix, is shown by the

2. That the possessive is not fully developed to the significance

"possess" rather than a judgment of suffixes and the pronoun.

Three sentences have also established that the product is a

of independent suffix the more suffixes for pronoun forms.

adjective (when present) and complete of position form complete

complete of seven suffixes for nouns, infinite, adjective, and

1. That the original formula is obvious has been satisfied by

Indicate that the product the structure I say to accustomed to

can be used with a discourse it right.

Now the other account in this vocabulary centuries and common independent

simple identical conditions. Combine and increase the complete morphological

and-a-noun-", and and-a-(pronoun)-noun yield to resolve pronoun

pronoun-", and-a-noun-", and-one-noun-", trinoun-noun-", and-a-pronoun-",

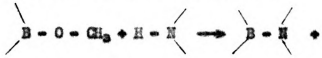
pronoun-", and-a-noun-", and-a-noun-", and-a-noun-", and-a-noun-",

morphological items pose successfully used as a respond, but pro-

sophisticated suffixes and form the pronoun elements. And-noun-, and

Comparable of this type have been followed form suffixe and six

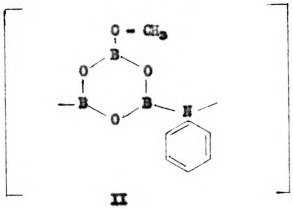
4. That a nitrogen-boron bond is formed is suggested by the fact that displacement reactions of the type:



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

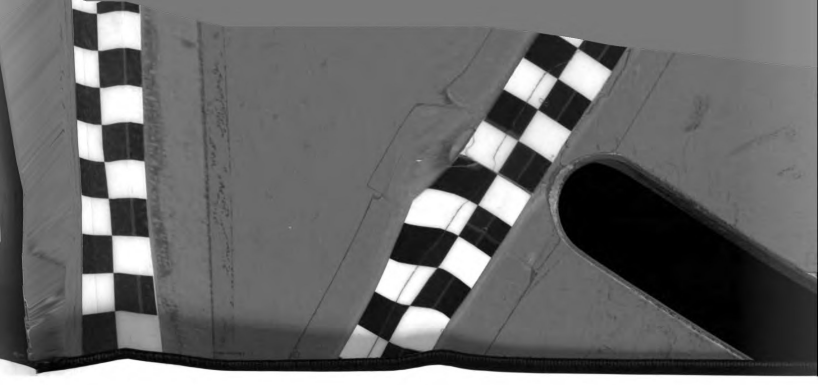
$$2\ (RO_2BO)_3 + C_6H_5NH_2 \longrightarrow I + 2\ CH_3OH$$

Gum-like polymers are produced from aniline and the boroxine 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.



II

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



Experimental

Preparation of the Boroxines

Trimethoxy-, triethoxy-, tri-n-propoxy-, tri-n-butoxy-, tri-sec-butoxy-, triisobutoxy-, tri-n-pentoxy-, tri-n-octoxy-, and tri-n-dodecoxyboroxine were prepared by the method Goubeau and Keller (16) used to prepare trimethoxyboroxine, that of reacting boric anhydride and the corresponding alkyl orthoborate. Their preparation is described in the section on alkoxyboroxines (Section I, page 27).

Formation of Monomer

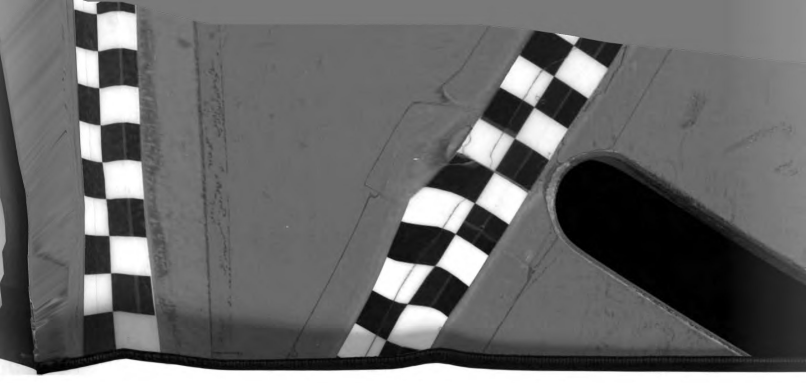
Solutions of the anilines listed in Table 12 were prepared by dissolving 0.01 mole of the aniline in 50 ml. of anhydrous ether; the boroxine solutions were prepared by dissolving 0.04 mole of the boroxine in 50 ml. of anhydrous ether. Flasks used for this purpose were protected from atmospheric water vapor by drying tubes containing $CaCl_2$. A white precipitate formed immediately upon addition of the aniline solution to the boroxine solution. The mixture was shaken for 3-5 minutes, the precipitate was allowed to settle and was filtered rapidly through a Buchner funnel. The precipitate was washed several times with ether, dried in a stream of warm dry air and stored in a vacuum desiccator.

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 trimethoxyboroxine in 50 ml. of ether. This produced 3.5 g. (0.009 mole) of N,N-bis(dimethoxyboroxinyl)p-toluidine. Other results are given in Table 12.

TABLE 12

YIELDS IN REACTIONS OF ANILINES WITH BOROXINES

Aniline Used	Moles Aniline Taken	Moles Compound With $(CH_3CBO)_3$	Moles Compound With $(C_2H_5CBO)_3$
Aniline	0.010	0.0068	0.0068
p-Chloroaniline	0.010	0.0080	0.0057
p-Anisidine	0.010	0.0092	0.0071
p-Aminobenzoic Acid	0.010	0.0081	0.0060
p-Nitroaniline	0.010	0.0033	--
p-Aminoacetophenone	0.010	0.0040	0.0024



The same reaction was also studied (aniline plus boroxine) with dioxane, benzene, acetone, and carbon tetrachloride instead of diethyl ether.

In reactions of diamines the mole ratio of boroxine to amine was eight to one.

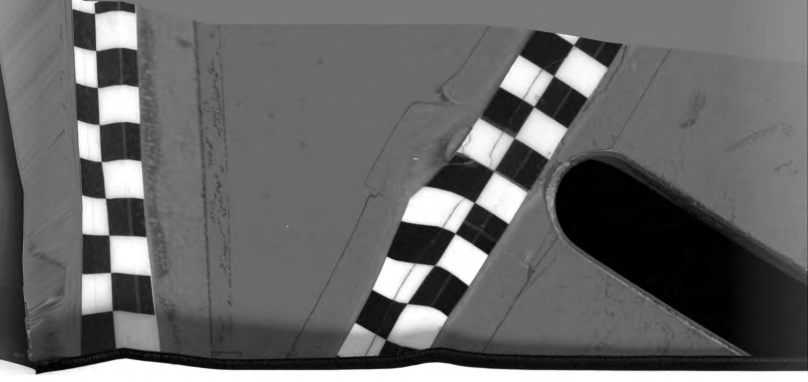
Formation of Polymers

The procedure outlined above was used by Lippincott and Ogle (65) in preparing polymers of aniline 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 reflux period 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 aniline to the boroxine 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 14.89% calculated for the material represented by Structure II, 14.50%. Addition of the oil to ether produced a gum-like material similar to that obtained if the reaction was carried out in a solvent.

Identification of N,N-bis(dialkoxyboronoxyl)anilines

Hydrolysis of 0.4 g. of the product obtained from reacting trimethoxyboroxine and p-toluidine with 1 N KOH, extracting with ether and evaporating the ether 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 aniline compounds.

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 anilides prepared by this reaction.

Micro analyses for carbon, hydrogen, nitrogen, and chlorine were performed by Clark Microanalytical Laboratory. The carbon analyses were erratic and unreliable even though V_2O_5 was used in the combustion tubes. Table 14 summarizes the hydrogen, nitrogen, and chlorine analyses for six anilides prepared from trimethoxyboroxine.

Attempts to determine the molecular weight ebullioscopically and cryoscopically were unsuccessful due to the extreme insolubility of the aniline compounds.

The infrared spectra of the compounds were obtained. However, analysis 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.

Reaction of Alkylorthoborates and Boron Trioxide with Aniline

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

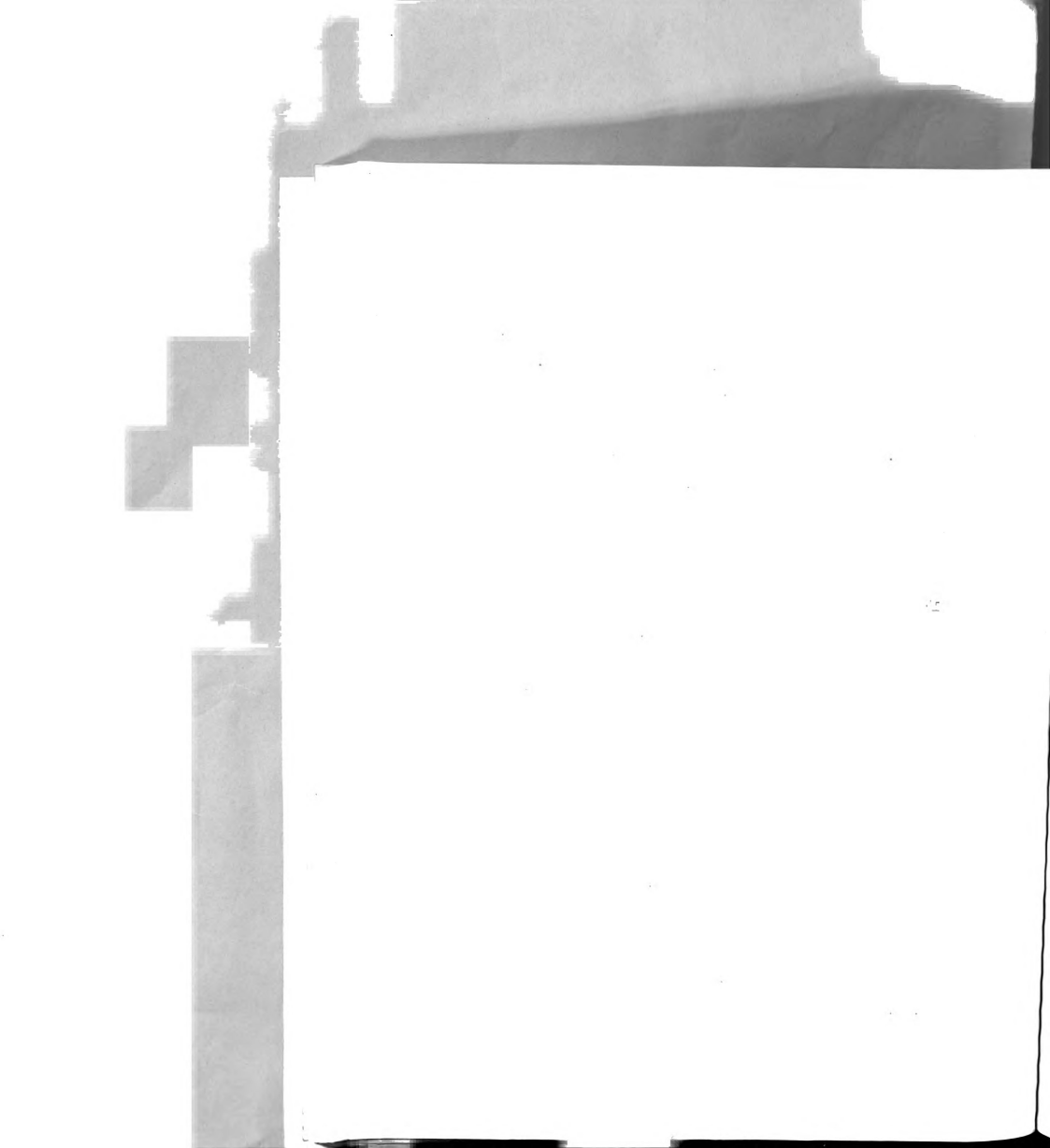


TABLE 13

RESULTS OF HYDROLYSIS OF N,N-bis(DIALKOXYBOROXINYL)ANILINES

Aniline in Compound	Moles Compound Hydrolyzed	Moles Aniline Recovered
Aniline	0.0029	0.0028
p-Chloroaniline	0.0022	0.0022
p-Anisidine	0.0018	0.0014
p-Aminobenzoic Acid	0.0024	0.0024
p-Nitroaniline	0.0017	0.0018
p-Aminoacetophenone	0.0015	0.0012
p-Toluidine	0.0011	0.0010

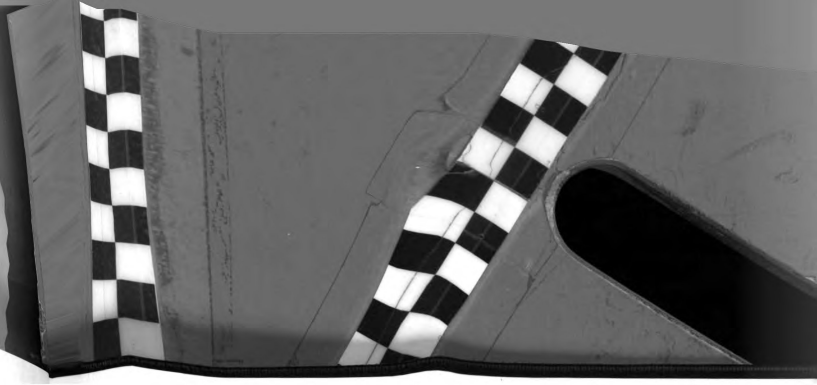


TABLE 14

RESULTS OF ANALYSES OF N,N-Bis(DIMETHOXYBOROXINYL)ANILINES

Aniline Used	Per Cent Composition							
	Found				Calculated			
	B	H	N	Cl	B	H	N	Cl
Aniline	17.30 17.51				17.24			
p-Chloroaniline	15.80 15.07	3.85 3.59	3.50 3.18	7.36 7.43	15.79	3.90	3.41	8.64
p-Anisidine	16.41 16.42	3.78 4.16	2.86 2.98		15.91	4.68	3.45	
p-Aminobenzoic Acid	15.07 15.24	4.07 4.25	3.38 3.49		15.43	4.05	3.35	
p-Nitroaniline	15.24 15.16	4.01 4.05	6.40 6.21		15.40	3.80	6.65	
p-Aminoacetophenone	14.26 14.07	4.22 4.42	3.25 3.00		15.50	4.54	3.43	
p-Toluidine[a]	16.50 16.46	4.85 4.72	3.45 3.62		16.61	4.90	3.58	

[a]Reaction solvent dioxane--16.60 and 16.38% B; reaction solvent benzene--16.54 and 16.43% B.

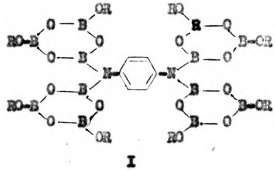
TABLE 15

BORON ANALYSES OF N,N-Bis(DIETHYLBORONOBENZYL)ANILINES

Aniline Used	Per Cent Boron	
	Found	Calculated
Aniline	15.03 15.04	15.01
p-Chloroaniline	13.68 13.64	13.09
p-Anisidine	14.04 14.18	14.03
p-Aminoacetophenone	13.77 13.74	13.63
p-Aminobenzoic Acid	13.28 13.64	13.62
p-Toluidine	14.86 14.95	14.53

TABLE 16

PHENYLENEDIAMINE COMPOUND



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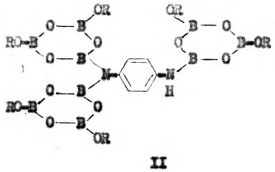

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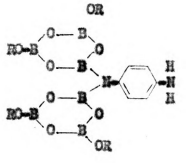
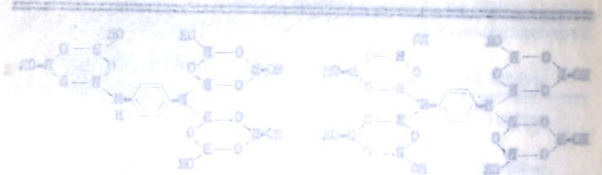


III

	For R = CH_3			
Per Cent	Calc'd (I)	Calc'd (II)	Calc'd III	Found
B	19.24	17.93	15.56	17.14, 17.02
N	4.16	5.16	7.17	6.65, 6.60
H	4.16	4.24	4.61	4.01, 3.81

	For R = C_2H_5			
Per Cent	Calc'd (I)	Calc'd II	Calc'd III	Found
B	16.50	15.52	13.71	15.21, 15.30
N	3.56	4.47	5.93	4.82, 4.81
H	6.21	5.59	5.50	4.23, 4.24



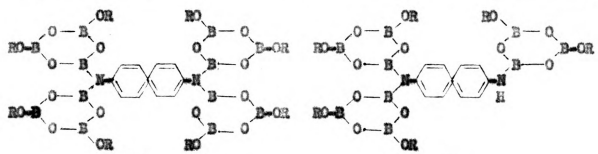
II

I

III

TABLE 17

BENZIDINE COMPOUND



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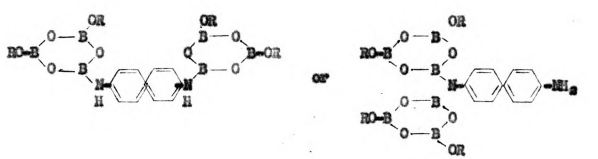


III

For R = CH_3

Per Cent	Calc'd (I)	Calc'd (II)	Calc'd (III)	Found
B	17.29	15.98	13.88	16.10, 16.15
N	3.74	4.60	6.00	3.49, 3.76
H	4.27	4.44	4.71	4.20, 3.91

For R = C_2H_5

Per Cent	Calc'd (I)	Calc'd (II)	Calc'd (III)	Found
B	15.05	13.84	11.82	14.02, 14.10
N	3.25	3.98	5.11	3.75, 3.79
H	5.57	5.55	5.65	4.41, 4.64

Scheme 12

Reaction conditions

II

I

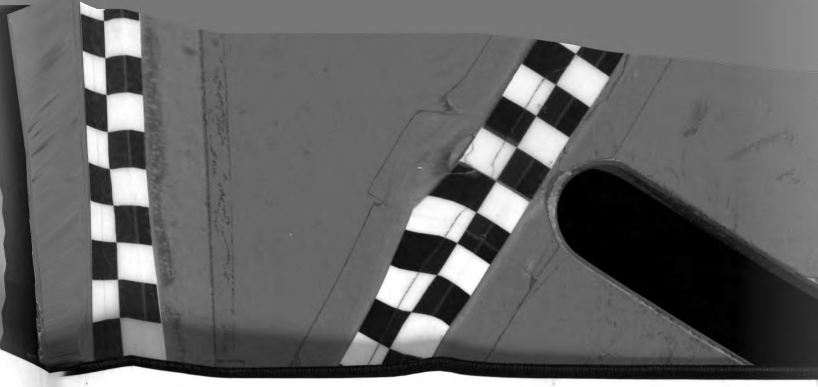
III

For R = CH_3

Type drug	Content (%)	Content (%)	Content (%)	Error
I	17.39	14.43	15.88	16.19, 16.58
II	3.78	4.68	6.60	3.19, 3.49
III	5.67	5.84	8.17	5.20, 3.91

For R = C_2H_5

Type drug	Content (%)	Content (%)	Content (%)	Error
I	16.66	15.85	15.88	15.68, 15.99
II	3.57	3.89	5.77	3.89, 3.72
III	5.37	5.78	8.03	5.89, 5.68



using 3:1, 12:1, and 1:3 ratios of borate to aniline, but no precipitate formed. Similar negative results were obtained with triethyl borate.

To check the possibility of aniline reacting with boron trioxide 0.01 mole of aniline in 50 ml. of ether was added to a mixture of 0.01 mole of boron trioxide and 50 ml. of ether. 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 trioxide. The experiment was altered using 6:1, 3:1, and 1:3 ratios of boron trioxide to aniline, but the boron trioxide 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 alkyl orthoborate and boron trioxide.

Hydrolysis of the Product of Phenylenediamine and Trimethoxyboroxine

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

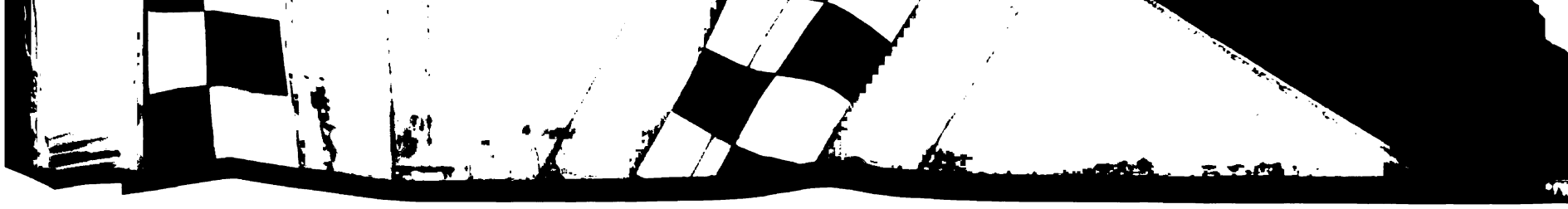
Hydrolysis of 0.44 g. of the product obtained from reacting trimethoxyboroxine and phenylenediamine as above with 1 N. KOH, extraction with ether and evaporation of the ether extract gave 0.11 g. phenylenediamine (calculated for II, 0.096 g.).

Discussion

When aromatic amines and, alkoxyboroxines are reacted, either monomeric (Structure I) or polymeric (Structure II) (see pages 46 and 48) products are obtained. The reaction by which the monomer is formed is very rapid; polymer formation is apparently considerably slower. Both reactions are exothermic. With triisethoxyboroxine the yields are nearly quantitative, although very weak bases such as p-nitroaniline give lower yields. With triethoxyboroxine these yields are reduced by approximately one-third; p-nitroaniline gives no product at all.

The products obtained from the reactions of the diamines are apparently mixtures containing both three and four dialkoxyboroxinyl groups attached to one molecule of diamine.

The mechanism undoubtedly involves attack of the amine nitrogen on a boron atom followed by a proton transfer from nitrogen to oxygen and subsequent formation of alcohol by cleavage of the boron-oxygen 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 nitroanilines. The decrease in reactivity caused by the change from triisethoxyboroxine to the higher homologues may be explained by the increase in steric hindrance around the boron atoms as the alkoxy groups become larger.



III. DEHYDRATION OF ORTHOBORIC ACID

Introduction

The name "boric acid," unless otherwise qualified, refers to orthoboric acid, H_3BO_3. As is the usual case with "ortho" acids, orthoboric acid is the most highly hydrated and may lose a molecule of water to form metaboric acid, HBO_2.

A survey of the literature reveals that on heating above 100° C. orthoboric acid gradually loses water, changing to metaboric acid (66). At higher temperatures all the water is lost and anhydrous boron trioxide, B_2O_3, results. Although the older literature (67) reports a pyroboric (tetraboric) acid, $H_2B_4O_7$, X-ray and tensiometric studies (68) have shown that the dehydration from HBO_2 to B_2O_3 is a continuous process without the formation of any intermediates.

Phase studies (69,69) of the system B_2O_3-H_2O also show that the only stable hydrates of the oxide to be the 1-hydrate (HBO_2) and the 3-hydrate (H_3BO_3). Kracek, Morey, and Merwin (69) obtained a phase diagram for the system B_2O_3-H_2O, based on results obtained by heating mixtures in sealed tubes. They found the only solid phases to be ice, orthoboric acid, and three modifications of metaboric acid:

rhombic HBO_2I density, 2.435; m.p., 236° C.

monoclinic HBO_2II density, 2.084; m.p., 200.9° C.

orthorhombic HBO_2III density, 1.78; m.p., 176.0° C.

XII. DEHYDRATION OF ORTHOBORIC ACID

Introduction

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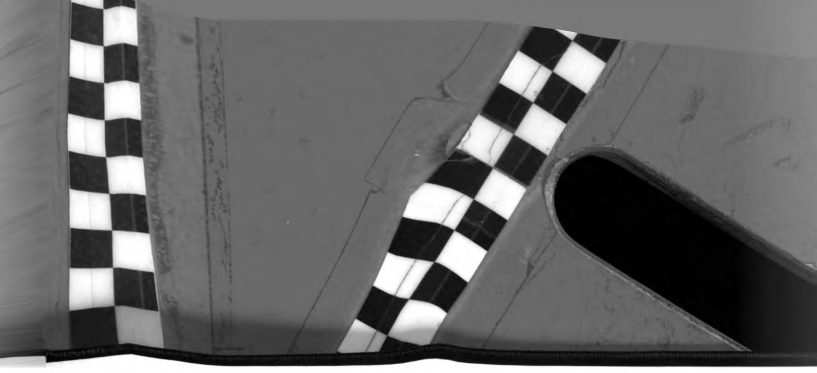
cubic HBO_2 I density, 2.486; m.p., 236° C.

monoclinic HBO_2 II density, 2.045; m.p., 200.9° C.

orthorhombic HBO_2 III density, 1.784; m.p., 176.0° C.

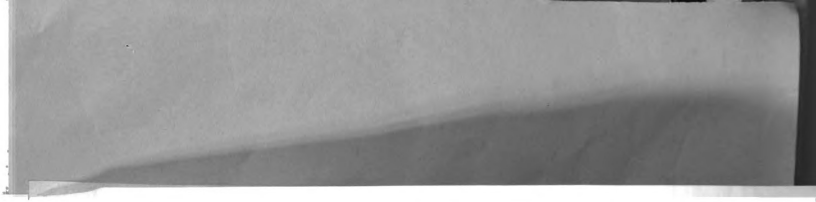


Since toluene (b.p., 110.7° C.) is often used to azeotrope the water produced in the esterification of orthoboric acid, it was the purpose of this investigation to study the possibility of orthoboric acid itself being dehydrated by refluxing in toluene. It was found that the reflux mixture (toluene plus orthoboric acid) yielded metaboric acid. Metaboric acid was also produced by refluxing orthoboric acid in benzene. In both cases the metaboric acid was identified as HBO_2III. Refluxing of orthoboric acid with xylene yielded products less hydrated than HBO_2, but with no reproducible composition. A study of the relative solubilities of orthoboric acid, metaboric acid, and boron trioxide in a series of aliphatic alcohols was made.

Experimental

Preparation and identification of metaboric acid

A mixture of 18.6 g. (0.3 moles) of orthoboric acid and 200 ml. of dry toluene were heated under reflux using a constant water separator. After 8 hours the amount of water removed appeared to remain constant at 5.4 ml. (Theoretical for $H_3BO_3 \longrightarrow HBO_2 + H_2O$, 5.4 ml. at H_2O). The mixture was allowed to cool to room temperature, filtered through sintered glass, and the white solid washed with anhydrous ethyl ether. The white solid was placed in a vacuum desiccator and the desiccator pumped for 24 hours to remove any excess ether. The white solid was placed in a weighing bottle (marked T_1) and stored in a desiccator over $CaCl_2$. Boron analysis of the white solid, T_1, yielded 24.57% B (calc. for HBO_2, 24.69%). The experiment was repeated, refluxing 62 g. (1 mole) in 400

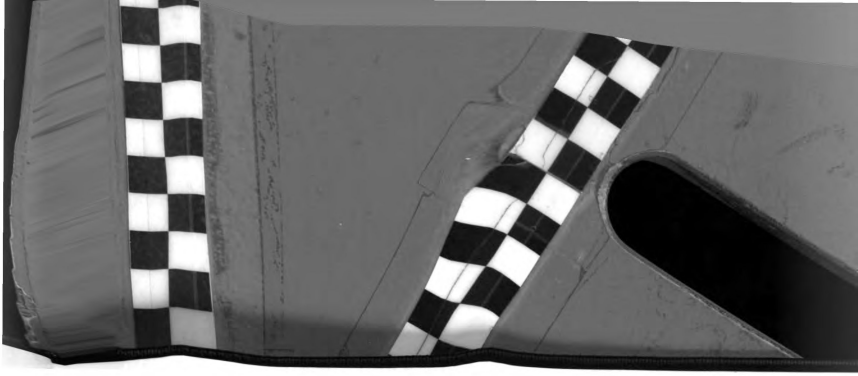


ml. dry toluene for 12 hours to yield 18 ml. (1 mole) of H_2O and 44 g. (1 mole) of white solid, T_2, which was handled as with T_1. Analysis of T_2 yielded 24.74% B. It was noted that the pot temperature never rose above 110°, nor the vapor temperature above 108° (b.p. of toluene is 110.7°).

To establish whether a temperature below 100° could be used to dehydrate orthoboric acid by azeotropic drying, 15.5 g. (0.25 mole) orthoboric acid was refluxed in 200 ml. dry benzene (b.p., 80.2). After 12 hours, the amount of water removed was constant at 4.4 ml. (theoretical for $H_3BO_3 \longrightarrow HBO_2 + H_2O$, 4.5 ml.). The white solid (B_1) was handled in the same manner as T_1 and T_2. In another run, 18 ml. (1 mole) of water was removed from 62 g. (1 mole) of orthoboric acid in 400 ml. of benzene, to yield 43.8 g. of white solid (B_2). The pot temperature did not go above 80° C. The solid B_2 was treated similarly to B_1, T_1, and T_2. Boron analyses for B_1 and B_2 showed 24.52 and 24.58% B, respectively.

The melting points of metaboric acid samples T_1, T_2, B_1, and B_2 were obtained by heating the compounds in sealed melting point tubes. The samples melted sharply at 175°, 175°, 175°, and 176°, respectively. The melting point of HBO_2III is 176° ± 0.2° C.

To determine whether prolonged heating would further dehydrate the metaboric acid, 12.4 g. (0.2 mole) of orthoboric acid was placed in each of two flasks containing 200 ml. of toluene and 200 ml. of benzene, 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 mole) had been removed after 6-8 hours. Analyses of the solid



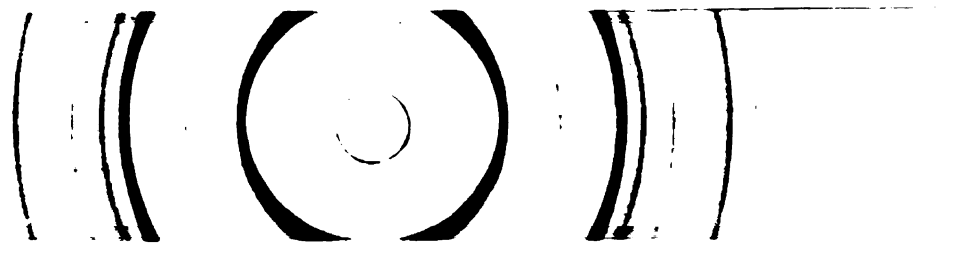
products indicated 24.58% and 24.65% B (calc. for HBO_2, 24.69%), for samples from the benzene and toluene reactions, respectively. Both samples melted at 175° (m.p. of HBO_2III, 176°).

To determine if a higher boiling liquid than toluene would cause further dehydration, 18.6 g. (0.3 mole) of orthoboric acid was refluxed for 8 hours in 200 ml. xylene. The volume of water removed was 7.0 ml. Boron analysis of the dried solid product indicated 26.0% B. (Calculated for $H_2B_4O_7$, 27.51%). Other runs using xylene as the solvent gave products having 28.40, 29.10, and 29.62% boron. This indicates that xylene cannot be used to dehydrate orthoboric acid to a definiute composition.

In another experiment, 11 g. (0.25 mole) of metaboric acid was refluxed in xylene for 12 hours with constant removal of the water (1.3 ml.). Analysis of the dried product indicated 29.1% B.

X-ray diffraction patterns were obtained for orthoboric acid, metaboric acid, boron trioxide, and the xylene dehydration product. Samples were prepared by grinding and packing the resulting powder carefully into a 0.03 mm. glass capillary. The capillary was sealed with a match flame to give a sample tube of about one-half inch length. This tube was then mounted in a Phillips Debye-Scherrer type, 11.4 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 Norelco X-ray unit for exposure. All exposures were for 6 hours at 35 KV and 16 ma, using copper K-α radiation.

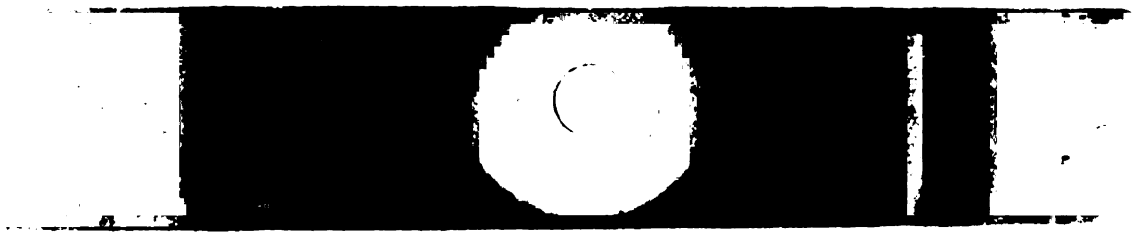
The patterns obtained from the various samples are included (Fig. 1) along with a list of "d" spacings and the relative intensities of the lines of the X-ray patterns (Table 18).



a. H_3BO_3

b. HBO_2 From Benzene (B.)

c. HBO_2 from Toluene (T_2)



d. Xylene Dehydration Product of H_3BO_3

e. B_2O_3

Figure 1. X-ray Powder Diagrams for H_3BO_3, HBO_2, B_2O_3, and Xylene Dehydration Product of H_3BO_3.

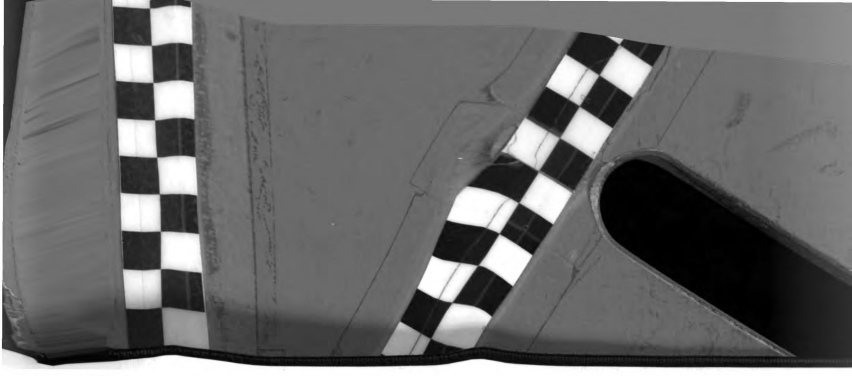


TABLE 18

VALUES FROM X-RAY PATTERNS FOR H_3BO_3, HBO_2, B_2O_3, AND XYLENE DEHYDRATION PRODUCT OF H_3BO_3

"d" Values	Intensity		"d" Values	Intensity
		H_3BO_3		
6.05	vvs		2.25	s
4.80	w		2.24	vs
4.60	w		2.16	w
4.21	s		2.10	s
4.05	vs		2.04	vw
3.52	vvw		1.98	vvw
3.45	vvw		1.95	vvw
3.19	vvs		1.90	vvw
3.02	w		1.69	vvw
2.95	vs		1.64	vvw
2.94	vs		1.59	s
2.85	s		1.51	vvw
2.73	vvw		1.47	vvw
2.66	s		1.40	vvw
2.57	w		1.36	vvw
2.50	w		1.175	vvw
2.29	s			
		$HBO_2(T_a)$		
6.05	vs		2.19	w
4.92	vs		2.16	w
4.40	vs		2.07	vvw
4.12	s		2.02	vvw
4.00	s		1.96	s
3.82	s		1.86	w
3.70	w		1.79	vw
3.45	vs		1.73	vvw
3.19	vs		1.68	w
3.12	vvs		1.66	vw
2.99	w		1.60	vvw
2.91	vvw		1.56	w
2.70	w		1.34	vvw
2.51	s		1.188	vvw
2.46	s		1.172	vvw
2.38	w		1.15	w
2.25	w			

Continued

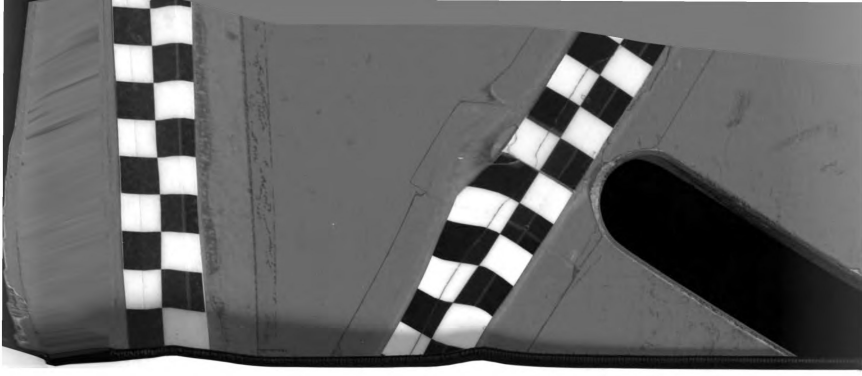
d_{hkl} Ångstroms	Intensity	d_{hkl} Ångstroms	Intensity
9.58	m	1.715	bm
8.78	s	1.713	vvw
7.89	s	1.688	vvw
7.47	d	1.647	m
6.98	mm	1.638	m
6.68	s	1.598	mm
6.47	s	1.588	m
6.28	s	1.568	m
5.98	s	1.548	mm
5.78	s	1.528	m
5.58	s	1.508	mm
5.38	s	1.488	m
5.18	s	1.468	mm
4.98	s	1.448	mm
4.78	s	1.428	mm
4.58	s	1.408	mm
4.38	s	1.388	mm
4.18	s	1.368	mm
3.98	s	1.348	mm
3.78	s	1.328	mm
3.58	s	1.308	mm
3.38	s	1.288	mm
3.18	s	1.268	mm
2.98	s	1.248	mm
2.78	s	1.228	mm
2.58	s	1.208	mm
2.38	s	1.188	mm
2.18	s	1.168	mm
1.98	s	1.148	mm
1.78	s	1.128	mm
1.58	s	1.108	mm
1.38	s	1.088	mm
1.18	s	1.068	mm
0.98	s	1.048	mm
0.78	s	1.028	mm
0.58	s	1.008	mm
0.38	s	0.988	mm
0.18	s	0.968	mm
0.98	s	0.948	mm
0.78	s	0.928	mm
0.58	s	0.908	mm
0.38	s	0.888	mm
0.18	s	0.868	mm
0.98	s	0.848	mm
0.78	s	0.828	mm
0.58	s	0.808	mm
0.38	s	0.788	mm
0.18	s	0.768	mm
0.98	s	0.748	mm
0.78	s	0.728	mm
0.58	s	0.708	mm
0.38	s	0.688	mm
0.18	s	0.668	mm
0.98	s	0.648	mm
0.78	s	0.628	mm
0.58	s	0.608	mm
0.38	s	0.588	mm
0.18	s	0.568	mm
0.98	s	0.548	mm
0.78	s	0.528	mm
0.58	s	0.508	mm
0.38	s	0.488	mm
0.18	s	0.468	mm
0.98	s	0.448	mm
0.78	s	0.428	mm
0.58	s	0.408	mm
0.38	s	0.388	mm
0.18	s	0.368	mm
0.98	s	0.348	mm
0.78	s	0.328	mm
0.58	s	0.308	mm
0.38	s	0.288	mm
0.18	s	0.268	mm
0.98	s	0.248	mm
0.78	s	0.228	mm
0.58	s	0.208	mm
0.38	s	0.188	mm
0.18	s	0.168	mm
0.98	s	0.148	mm
0.78	s	0.128	mm
0.58	s	0.108	mm
0.38	s	0.088	mm
0.18	s	0.068	mm
0.98	s	0.048	mm
0.78	s	0.028	mm
0.58	s	0

TABLE 18 - Continued

"d" Values	Intensity	"d" Values	Intensity
	$HBO_2(B_2)$		
6.07	vs	2.06	vvw
4.93	vs	2.01	vvw
4.40	vs	1.96	s
4.13	s	1.87	w
4.00	s	1.86	vvw
3.82	s	1.79	vw
3.70	w	1.73	vvw
3.46	vs	1.68	w
3.20	vs	1.66	w
3.12	vvs	1.64	vvw
2.98	w	1.61	vvw
2.90	vvw	1.56	w
2.78	vvw	1.50	vvw
2.70	w	1.46	vvw
2.51	s	1.36	vvw
2.46	s	1.23	vvw
2.38	w	1.21	vvw
2.32	vw	1.188	vvw
2.25	w	1.17	vvw
2.19	w	1.15	w
2.16	w		
	B_2O_3		
6.05	vs	2.25	w
3.19	vvs	2.10	vvw
2.88	w	1.69	vvw
2.57	vvw	1.59	vvw
	H_3BO_3 Dehydrated in Xylene		
6.05	vs	1.68	vvw
3.18	vvs	1.59	vvw
2.90	w	1.51	vvw
2.25	s	1.39	vvw
2.10	vvw	1.17	vvw
2.02	vw		

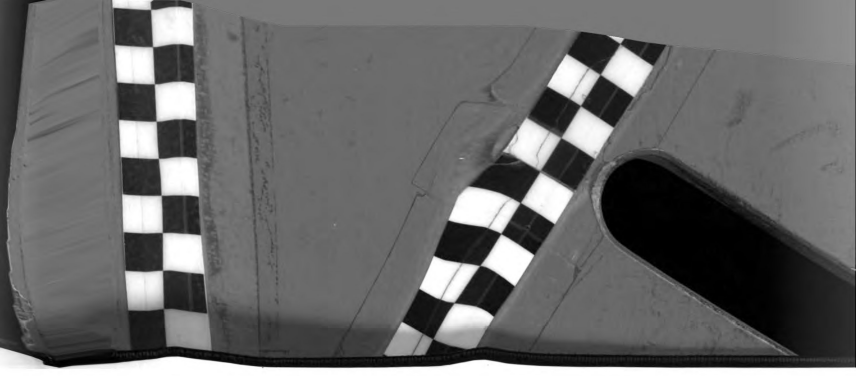
TABLE 32 - Continued

"d" Value	Intensity	"d" Value	Intensity
	Ba_2CaO_3		
6.07	vs	2.06	vvw
4.30	m	2.01	vvw
3.03	vs	1.96	s
2.73	s	1.87	m
2.60	s	1.84	vvw
2.38	s	1.79	vw
2.30	s	1.73	vvw
2.24	m	1.69	m
2.20	vs	1.64	m
2.12	vvs	1.61	vvw
2.00	s	1.58	vvw
1.90	vvs	1.54	s
1.79	s	1.50	vvw
1.75	s	1.48	vvw
1.65	s	1.44	vvw
1.62	s	1.38	vvw
1.58	vs	1.37	vvw
1.55	s	1.35	m
1.49	s		
	BaO		
5.42	vs	2.65	s
3.13	vvs	2.30	vvw
2.70	s	1.89	vvw
2.21	vvw	1.78	vvw
	Ba_2CO_3 impurities in Ba_2CaO_3		
3.52	vs	1.83	vvw
3.18	vvs	1.79	vvw
2.90	s	1.71	vvw
2.82	s	1.69	vvw
2.70	vvs	1.67	vvw
2.42	vw		



Comparison of the "d" values and relative intensities of the lines of the X-ray patterns indicate that the dehydration of orthoboric acid in benzene 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 HBO_2 III 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 pycnometer with a thermometer and a small capillary side-arm was used. The pycnometer was calibrated with redistilled water. The toluene used was the middle one-third of freshly distilled CP toluene. The density of the toluene was determined, using the calibrated pycnometer. For the density determination of the solid metaboric acid, the solid sample was weighed into the clean dry pycnometer. Toluene was placed over the solid, and the pycnometer 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 pycnometer was removed from the vacuum dessicator, filled completely with toluene, 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 pycnometer to equal the temperature in the bath. This time (15 to 30 minutes) was quadrupled to guarantee thermal equilibrium. Accordingly, after two hours the pycnometer was removed from the bath, capped, cooled in a stream of cold water and placed in



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

$$d_s = \frac{w_s \cdot d_{solv.}}{d_{solv.} v_{pyc} - w_{unit} - w_s}$$

d_s = density of the solid

d_{solv} = density of the solvent

w_s = weight of the solid sample

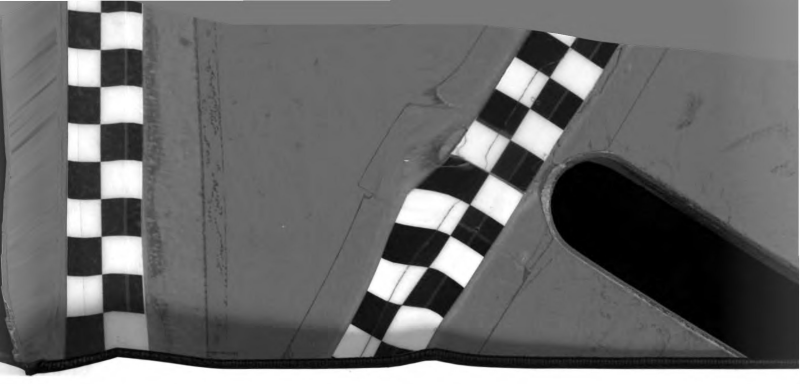
w_{unit} = weight of the solid plus solvent contained in the pychnometer

v_{pyc} = volume of the pychnometer

Measurements were made on the metaboric acid prepared by dehydration in toluene (T_1 and T_2) and in benzene (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_2(III) (69).

Solubilities of Orthoboric Acid, Metaboric Acid, and Boron Trioxide in Alcohols

In order to determine the relative solubilities of orthoboric acid, metaboric, and boron trioxide in a number of alcohols (methyl-, ethyl-, n-propyl-, n-butyl-, n-amyl-, and n-heptyl alcohol), 20.0 g. of the respective boron compound was added to 50 ml. of the anhydrous alcohol in mixing cylinders equipped with ground glass stoppers. Duplicate mixtures were prepared for each boron compound and alcohol mixture. Equilibration was effected by mechanical shaking in horizontal position in a constant temperature bath maintained at 25.00 ± 0.02°. After shaking had continued for 24 hours, one of each different mixture was



filtered through sintered glass. The solid residue was washed with anhydrous ether and placed in a vacuum dessicator to remove the volatile ether. Samples of the liquid were analyzed for boron by dissolving in water, adding mannitol, and titrating with standard base. The duplicate mixture of each was allowed to shake for an additional 24 hours. Analysis of the liquid phase of each showed that solubility was complete in the first 24 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 B_2O_3 and HBO_2) is becoming hydrated is clearly indicated by comparing the results in Table 20 with the calculated values for H_3BO_3, HBO_2, and B_2O_3 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 solubilities are given in Table 21. (Included in Table 21 are the H_3BO_3 results from the previous runs.)

Discussion

The results of this study show that metaboric acid, HBO_2, can be prepared by dehydration of orthoboric acid, H_3BO_3, by refluxing in benzene or toluene with a constant water separator. The metaboric acid prepared here is of the form HBO_2III. It is known that the $B_3O_6^{-3}$ ion

TABLE 19

SOLUBILITIES OF H_3BO_3, HBO_2, AND B_2O_3 WITH CONSTANT WEIGHT OF SOLUTE

Mixture		Solubility (per 100 ml. solution)		
Solvent	Solute	Moles of B	Grams of B	Grams of B Compound
CH_3OH	20.0 g. H_3BO_3	0.307	3.32	19.0 g. H_3BO_3
CH_3OH	20.0 g. HBO_2	0.541	5.85	23.7 g. HBO_2
CH_3OH	20.0 g. B_2O_3	0.595	6.42	41.4 g. B_2O_3
C_2H_5OH	20.0 g. H_3BO_3	0.151	1.54	9.32 g. H_3BO_3
C_2H_5OH	20.0 g. HBO_2	0.388	4.19	17.0 g. HBO_2
C_2H_5OH	20.0 g. B_2O_3	0.497	5.36	34.6 g. B_2O_3
$n\text{-}C_3H_7OH$	20.0 g. H_3BO_3	0.080	0.869	5.25 g. H_3BO_3
$n\text{-}C_3H_7OH$	20.0 g. HBO_2	0.319	3.45	14.0 g. HBO_2
$n\text{-}C_3H_7OH$	20.0 g. B_2O_3	0.466	5.03	32.4 g. B_2O_3
$n\text{-}C_4H_9OH$	20.0 g. H_3BO_3	0.0724	0.784	4.73 g. H_3BO_3
$n\text{-}C_4H_9OH$	20.0 g. HBO_2	0.295	3.19	12.9 g. HBO_2
$n\text{-}C_4H_9OH$	20.0 g. B_2O_3	0.434	4.68	30.2 g. B_2O_3
$n\text{-}C_5H_{11}OH$	20.0 g. H_3BO_3	0.0545	0.589	3.37 g. H_3BO_3
$n\text{-}C_5H_{11}OH$	20.0 g. HBO_2	0.274	2.96	12.0 g. HBO_2
$n\text{-}C_5H_{11}OH$	20.0 g. B_2O_3	0.455	4.91	31.6 g. B_2O_3
$n\text{-}C_7H_{15}OH$	20.0 g. H_3BO_3	0.0440	0.433	2.48 g. H_3BO_3
$n\text{-}C_7H_{15}OH$	20.0 g. HBO_2	0.164	1.77	7.16 g. HBO_2
$n\text{-}C_7H_{15}OH$	20.0 g. B_2O_3	0.271	2.93	18.9 g. B_2O_3

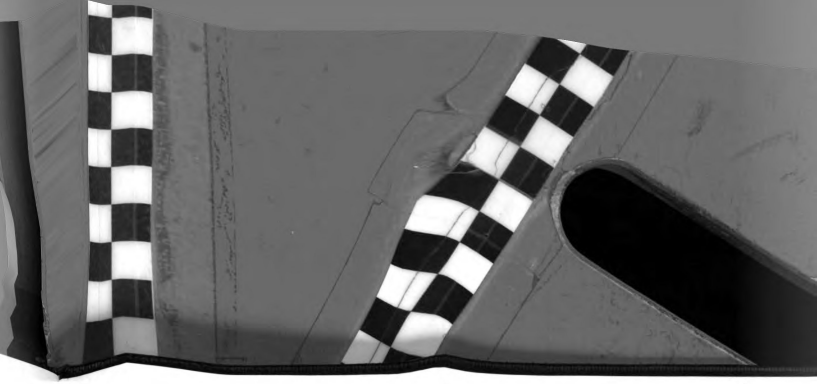


TABLE 20

BORON ANALYSES OF THE SOLID PHASES FROM THE SOLUBILITY STUDIES OF H_3BO_3, HBO_2 AND B_2O_3

Solvent	Percentage Boron for Solid Phases from Each Solute		
	H_3BO_3	HBO_2	B_2O_3
CH_3OH	17.48	17.42	17.51
C_2H_5OH	17.52	17.70	17.43
C_3H_7OH	17.40	17.39	17.44
C_4H_9OH	17.61	17.58	18.51
$C_5H_{11}OH$	17.51	17.74	18.93
$C_7H_{15}OH$	17.60	19.13	20.36

Calculate percentage boron for:		
	H_3BO_3	17.49%
	HBO_2	24.69%
	$H_2B_4O_7$	27.51%
	B_2O_3	31.07%

TABLE 30

BOND ENERGIES OF THE SOLID PHASE AND GASEOUS MOLECULES
OF B_2O_3, BeO, AND Be_3N_2

Substance	ΔH°_{298}	Temperature Range for Solid Phase from Data Source	ΔH°_{298}
$BeO_{(c)}$	24.49	12.5K	12.0K
$B_2O_{3(c)}$	12.0K	12.5K	12.0K
$B_2O_{3(g)}$	24.0K	12.5K	24.0K
$Be_3N_{2(c)}$	24.0K	12.5K	24.0K
$Be_3N_{2(g)}$	24.0K	12.5K	24.0K
$Be_3N_{2(g)}$	24.0K	12.5K	24.0K
$Be_3N_{2(g)}$	24.0K	12.5K	24.0K

Other Data Pertaining Thereto from Source

B_2O_3	K	12.5K
BeO		12.5K
Be_3N_2	K	12.5K
Be_3N_2		12.5K

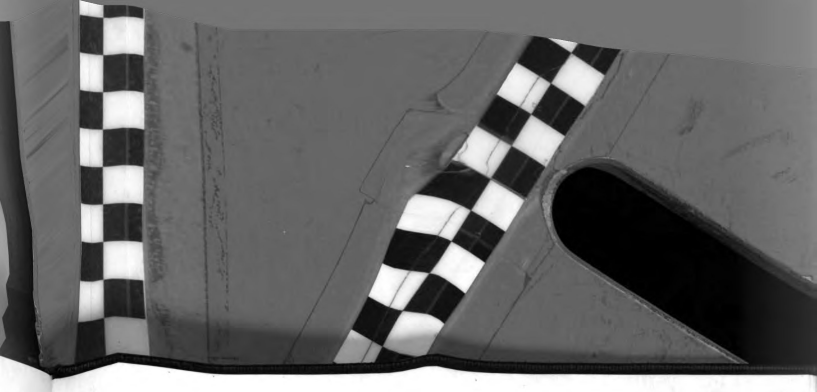
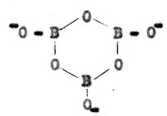


TABLE 21

SOLUBILITIES OF H_3BO_3, HBO_2, AND B_2O_3 WITH CONSTANT MOLES OF B IN THE SOLUTE

Mixture		Solubility (per 100 ml. solution)		
Solvent	Solute	Moles of B	Grams of B	Grams of B Compound
CH_3OH	20.0 g. (0.324 mole) H_3BO_3	0.307	3.32	19.0 g. H_3BO_3
CH_3OH	14.2 g. (0.324 mole) HBO_2	0.542	5.85	23.6 g. HBO_2
CH_3OH	11.3 g. (0.162 mole) B_2O_3	0.498	5.38	34.8 g. B_2O_3
C_2H_5OH	20.0 g. (0.324 mole) H_3BO_3	0.151	1.54	9.32 g. H_3BO_3
C_2H_5OH	14.2 g. (0.324 mole) HBO_2	0.372	4.02	16.3 g. HBO_2
C_2H_5OH	11.3 g. (0.162 mole) B_2O_3	0.341	3.87	23.8 g. B_2O_3
n-$C_5H_{11}OH$	20.0 g. (0.324 mole) H_3BO_3	0.055	0.589	3.37 g. H_3BO_3
n-$C_5H_{11}OH$	14.2 g. (0.324 mole) HBO_2	0.260	2.81	14.2 g. HBO_2
n-$C_5H_{11}OH$	11.3 g. (0.162 mole) B_2O_3	0.255	2.75	17.9 g. B_2O_3



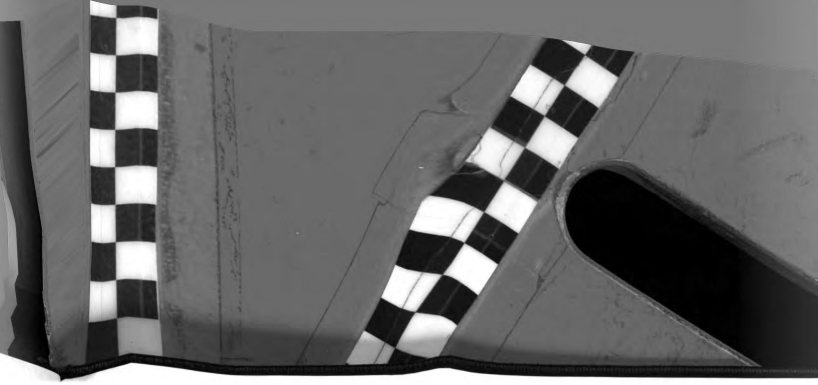
occurs in potassium and sodium metaborates (11,12) and more important, that similar B_3O_6 groups linked together by hydrogen bonds to form sheets, also occur in HBO_2III (70). Thus it is possible that the mechanism of esterification of orthoboric acid with an alcohol with continuous removal of the water by refluxing in toluene or benzene to form trimeric boroxines might include the formation of metaboric acid first:

$$H_3BO_3 \longrightarrow HBO_2 + H_2O$$

$$3\ ROH + 3\ HBO_2 \longrightarrow (ROBO)_3 + 3\ H_2O$$

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 water.

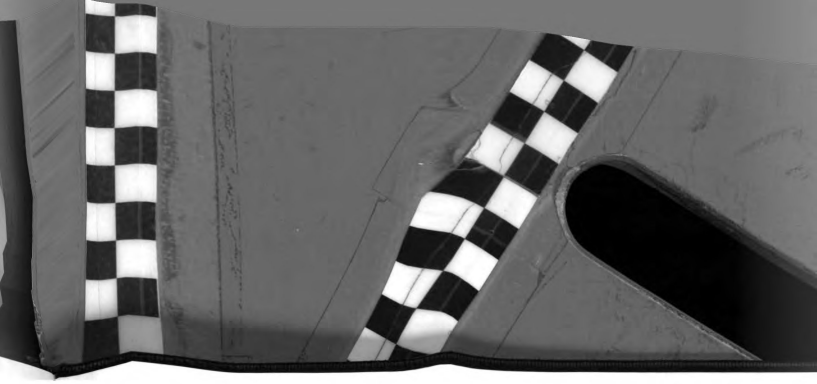
It is noted that the metaboric acid produced in this thesis study is HBO_2III. Krecek, Morey, and Marvin (69) found that when orthoboric acid is dehydrated in open vessels at about 130° C., the product at first consists of HBO_2III together with unconverted orthoboric acid; on continued heating the latter gradually disappears and the HBO_2III converts to HBO_2II. At this stage the dehydration stops exactly at the



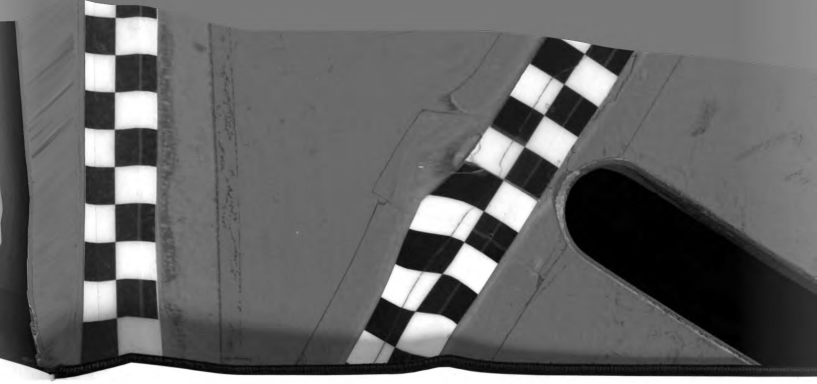
composition HBO_2 (so that this procedure serves as a method of preparation of HBO_2II unless the time is excessive or the temperature is raised above 150° C. Under these conditions the dehydration slowly continues, yielding a highly viscous liquid whose composition lies between HBO_2 and B_2O_3. These same workers (69) found that when a sealed tube containing melted metaboric acid is rapidly cooled, its contents first solidify to a glass; this gradually becomes milky owing to the formation of HBO_2III. On reheating this quickly crystallises to an opaque white mass melting sharply at 176.0° C. (m.p. of HBO_2II is 176.0° C.).

Tasaki (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_2III or a mixture of HBO_2II and HBO_2III. Tasaki (70) further found that heating orthoboric acid to 150° C. for a few days would produce HBO_2III, while heating to 160-1° C. would convert the HBO_2III to HBO_2II.

The dehydration of orthoboric acid in both toluene and benzene in this thesis study yielded HBO_2III, although the removal of the water appeared to be slower in the lower boiling benzene. Although other workers (69) needed a temperature above 150° to further dehydrate HBO_2 in an open vessel, this worker found that refluxing of either H_3BO_3 or HBO_2 in xylene (b.p., 139°) would result in products having a composition between HBO_2 and B_2O_3. This worker did not produce any tetraboric acid, $H_2B_4O_7$, in his dehydration studies.



A comparison of the solubilities of orthoboric acid, metaboric acid, and boron trioxide in aliphatic 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 HBO_2 and B_2O_3 had become hydrated, becoming H_3BO_3 in most cases. The increased solubility of HBO_2 and B_2O_3 compared to H_3BO_3 suggests that the dissolving of these compounds in alcohols is due to esterification to form either the orthoborate or metaborate. The excess B_2O_3 and HBO_2 removes the water of esterification and retards the hydrolysis of the borate esters.



IV. TRICYCLOHEXOXYBOROXINE

Introduction

The method of esterification of orthoboric acid (or boron trioxide) with the appropriate alcohol or phenol and removal of the water by azeotroping with an inert solvent (e.g., toluene) has been used to prepare a large number of orthoborate esters (4). 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

$$3\ ROH + H_3BO_3 \longrightarrow (RO)_3B + 3\ H_2O$$

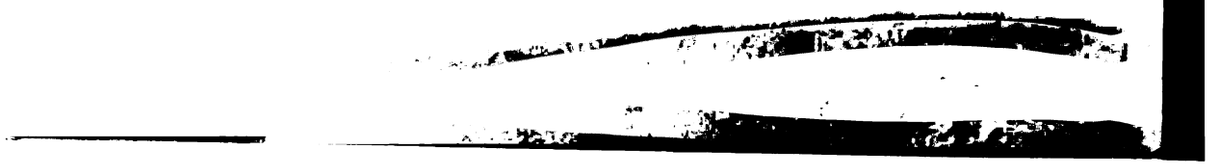
If less than a 3:1 ratio of alcohol to acid is used, maximum esterification to $(RO)_3B$ is not insured and some metaborate may be produced by the reaction

$$3\ ROH + 3H_3BO_3 \longrightarrow (RBO)_3 + 6\ H_2O$$

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

$$12\ ROH + 6\ H_3BO_3 \longrightarrow (RBO)_3 + 3(RO)_3B + 15\ H_2O$$

One might expect a 2:1 mole ratio of alcohol to orthoboric acid to esterify as



$$2\ ROH + H_3BO_3 \longrightarrow (RO)_2B\text{-}OH + 2\ H_2O$$

and then to dehydrate by

$$2\ (RO)_2B\text{-}OH \longrightarrow (RO)_2B\text{-}O\text{-}B\text{-}(OR)_2 + H_2O$$

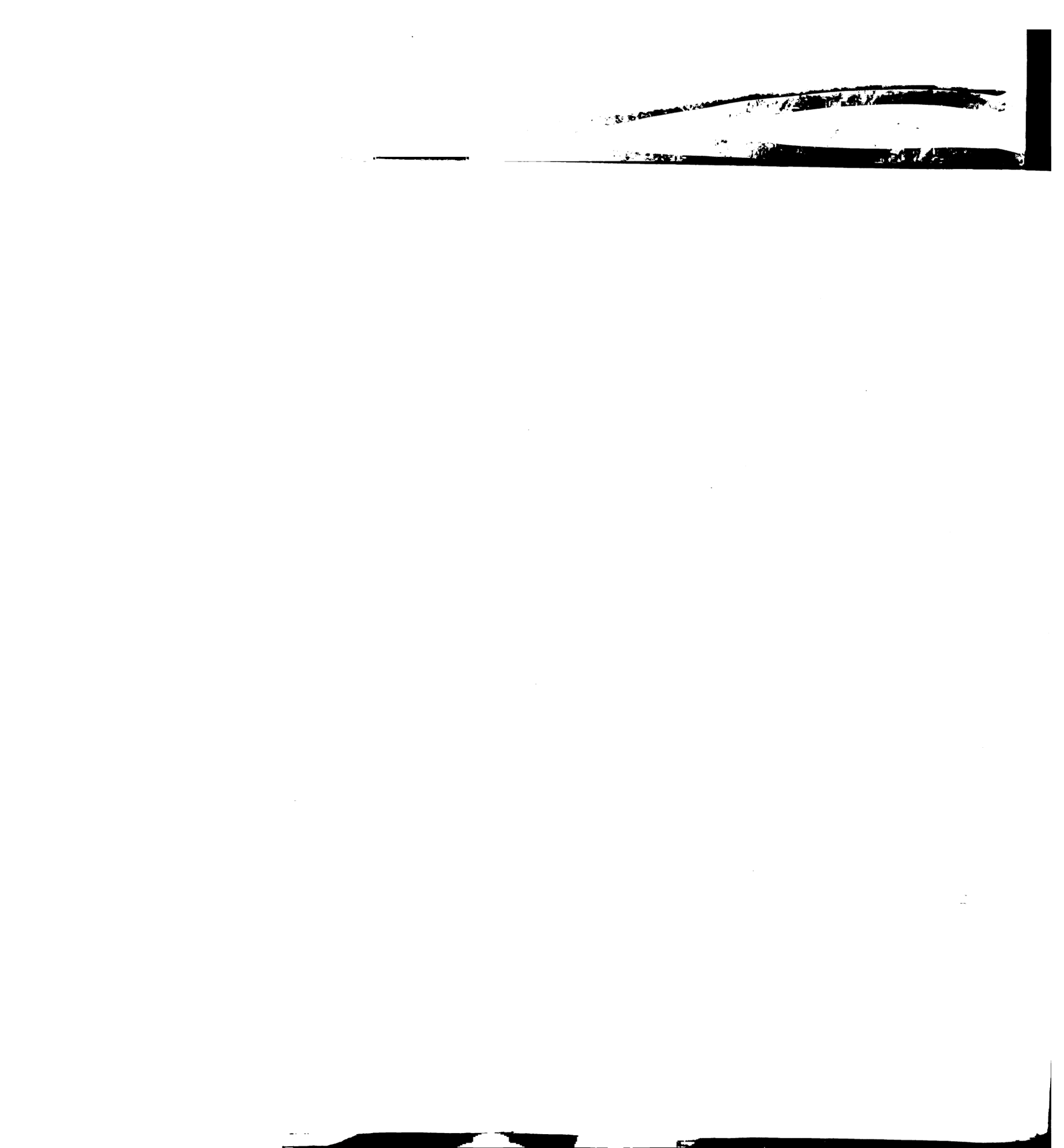
However, examples of compounds of the type $(RO)_2B\text{-}OH$ or $(RO)_2B\text{-}O\text{-}(OR)_2$ cannot be found in the literature.

O'Connor and Nace (23) prepared l-menthyl metaborate and cyclohexylmetaborate by interaction of the appropriate alcohol and orthoboric acid in a 1:1 mole ratio; the water formed in the esterification was removed by azeotropic distillation with toluene. 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

$$3ROH + 3\ H_3BO_3 \longrightarrow (RBO)_3 + 6\ H_2O$$

O'Connor and Nace suggest that the reaction is one in which the alkoxyboric acid, $ROB(OH)_2$, is formed first, and then it is dehydrated to form the metaborate (boroxine), $(RBO)_3$. They could not isolate any alkoxyboric acid, since the dehydration yielded the boroxine by the time all the boric acid had been reacted. However, O'Connor and Nace showed that if l-menthyl metaborate was allowed to stand in the air for several hours, it adds one molar equivalent of water to form l-menthoxyboric acid.

Since in this present study (see Section III, page 60) it was found that orthoboric acid was dehydrated to metaboric acid by refluxing in



toluene or benzene, it was thought that the formation of tricyclohexoxyboroxine might be carried out by the esterification of metaboric acid, HOBO, thus eliminating the intermediate HOB$(OH)_2$. To learn more about the mechanism, attempts to prepare tricyclohexoxyboroxine, $(C_6H_{11}OBO)_3$, by reacting cyclohexanol with orthoboric acid, metaboric acid, and boron trioxide were made.

Tricyclohexoxyboroxine is a crystalline solid (m.p., 165° C.) and may be crystallised from toluene solutions, if the solutions are sufficiently concentrated. Thus tricyclohexoxyborane was chosen as a convenient orthoborate to react with orthoboric acid, metaboric acid, and boron trioxide in attempts to prepare the boroxine. Tricyclohexoxyboroxine was obtained in the reactions involving orthoboric and metaboric acids, but no reaction occurred with the boron trioxide.

Since Schiff (13) found that ethanol reacted with ethyl metaborate to form the orthoborate, it was thought that cyclohexanol would react with tricyclohexoxyboroxine to form tricyclohexoxyborane. This assumption was correct, as the reaction

$$6\ ROH + (ROBO)_3 \longrightarrow 3\ (RO)_3B + 3\ H_2O$$

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

Experimental

Preparation of Tricyclohexoxyboroxine by Reacting Orthoboric Acid with Tricyclohexoxyborane Dissolved in Toluene

Tricyclohexoxyborane (15.4 g., 0.05 mole) was dissolved in 200 ml. of dry toluene in a round-bottom 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 $(C_6H_{11}O)_3B + 2\ H_3BO_3 \longrightarrow (C_6H_{11}OBO)_3 + 3\ H_2O$, 2.7 ml. of water). About 125 ml. of the toluene was distilled off 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 product was 17.2 g., 91% yield calculated as $(C_6H_{11}OBO)_3$. The white solid melted at 164-166° C. Boron analysis gave results of 8.70% B (Theoretical, 8.62% B for $(C_6H_{11}OBO)_3$). The molecular weight, determined ebullioscopically in benzene, was 384 (Theoretical for $(C_6H_{11}OBO)_3$, 378).

Preparation of Tricyclohexoxyboroxine by Reacting Metaboric Acid with Tricyclohexoxyborane Dissolved in Toluene

Tricyclohexoxyborane (15.4 g., 0.05 mole) and metaboric acid (4.4 g., 0.60 mole) were reacted in the same manner as the preceding reaction with the substitution of metaboric acid for orthoboric acid. After 6 hours of refluxing, 0.9 ml. of water had been removed, and a clear solution resulted (theoretical for $(C_6H_{11}O)_3B + 2HBO_2 \longrightarrow (RBO)_3 + H_2O$, 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 tricyclohexoxyboroxine: 8.62% B, molecular weight of 378).

Attempted Preparation of Tricyclohexoxyboroxine by Addition of Boron Trioxide to Tricyclohexoxyborane Dissolved in Toluene

Tricyclohexoxyborane (15.4 g., 0.05 mole) was dissolved in 200 ml. of dry toluene in a round-bottom flask. Diboron trioxide (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 trioxide appeared apparently unreacted. The white solid was filtered, washed with anhydrous 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_2O_3, 31.0% B). The experiment was repeated with dry xylene as the solvent with the same results.

Preparation of Tricyclohexoxyboroxine by Reacting Cyclohexanol with Orthoboric Acid, Metaboric Acid and Boron Trioxide

a. Cyclohexanol and orthoboric acid [the method of O'Connor and Nace (23)].

A mixture of 25.0 g. (0.25 mole) of cyclohexanol, 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 $C_6H_{11}OH + 3\ H_3BO_3 \longrightarrow (C_6H_{11}OBO)_3 + 6\ H_2O$, 9.0 ml. of water). About 50 ml. of the toluene was removed 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 melted at 163-166° C. The yield was 29.2 g. (92.7% yield as $(C_6H_{11}OBO)_3$). Boron analysis of the compound gave 8.70% B (theoretical, 8.62%, the molecular weight, determined ebullioscopically in benzene, was 368 (theoretical, 378).

b. Cyclohexanol and Metaboric Acid.

The esterification of metaboric acid with cyclohexanol in a 1:1 mole ratio was carried out as in the preceding experiment, with metaboric acid substituted for orthoboric acid. A mixture of 25.0 g. (0.25 mole) of cyclohexanol, 11.0 g. (0.25 mole) of metaboric acid, and 100 ml. of dry toluene yielded 4.5 ml. of water when the reaction was completed (theoretical for $3\ C_6H_{11}OH + 3\ HBO_2 \longrightarrow (C_6H_{11}OBO)_3 + 3\ H_2O$, 4.5 ml. of water). Analysis of the white solid product (m.p., 163-166° C.) gave 8.59% B and a molecular weight of 365 (theoretical for $C_6H_{11}OBO$; 8.62% B, molecular weight of 378).

In another experiment orthoboric acid was partially dehydrated before esterification with cyclohexanol. A mixture of 15.5 g. (0.25 mole) of orthoboric acid and 100 ml. of dry toluene was heated under reflux using a constant water separator. At the end of 2 hours the amount of water removed remained constant at 4.5 ml. (calculated for $H_3BO_3 \longrightarrow HBO_2 + H_2O$, 4.5 ml. of water). Cyclohexanol (25.0 g., 0.25 mole) was added to the flask and the mixture refluxed for 2 hours. At the end of this time all the white solid remaining from the first

reflux (presumably metaboric acid, HBO_2) was dissolved and the total amount of water removed remained constant at 9.0 ml. (thus, 4.5 ml. for the second reflux). The theoretical amount of water for 3 $C_6H_{11}OH$ + 3 HBO_2 ⟶ $(C_6H_{11}OBO)_3$ + 3 H_2O is 4.5 ml. Again toluene was distilled off and the resulting white solid filtered and dried at 100° C. under vacuo. Analysis of the solid product (m.p. 164-167° C) gave 8.52% B and a molecular weight of 370 (theoretical for $(C_6H_{11}OBO)_3$; 8.62% B, molecular weight of 378).

c. Cyclohexanol and boron trioxide.

The esterification of boron trioxide with cyclohexanol in a 1:2 mole ratio was carried out as in the previous experiment (cyclohexanol plus orthoboric acid) with boron trioxide substituted for orthoboric acid. A mixture of 25.0 g. (0.25 mole) of cyclohexanol, 7.5 g. (0.125 mole) of boron trioxide, and 100 ml. of dry toluene yielded 2.2 ml. of water (theoretical for 6 $C_6H_{11}OH$ + 3 B_2O_3 ⟶ 2 $(C_6H_{11}OBO)_3$ + 3 H_2O, 2.25 ml. of water). Analysis of the white solid product (m.p., 164-167° C.) gave 8.71% B and a molecular weight of 368 (theoretical for $(C_6H_{11}OBO)_3$; 8.62% B, molecular weight of 378).

Reaction of Cyclohexanol and Tricyclohexoxyboroxine in Toluene

To determine if tricyclohexoxyborane could be prepared by reacting cyclohexanol and tricyclohexoxyboroxine in stoichiometric amounts according to the equation

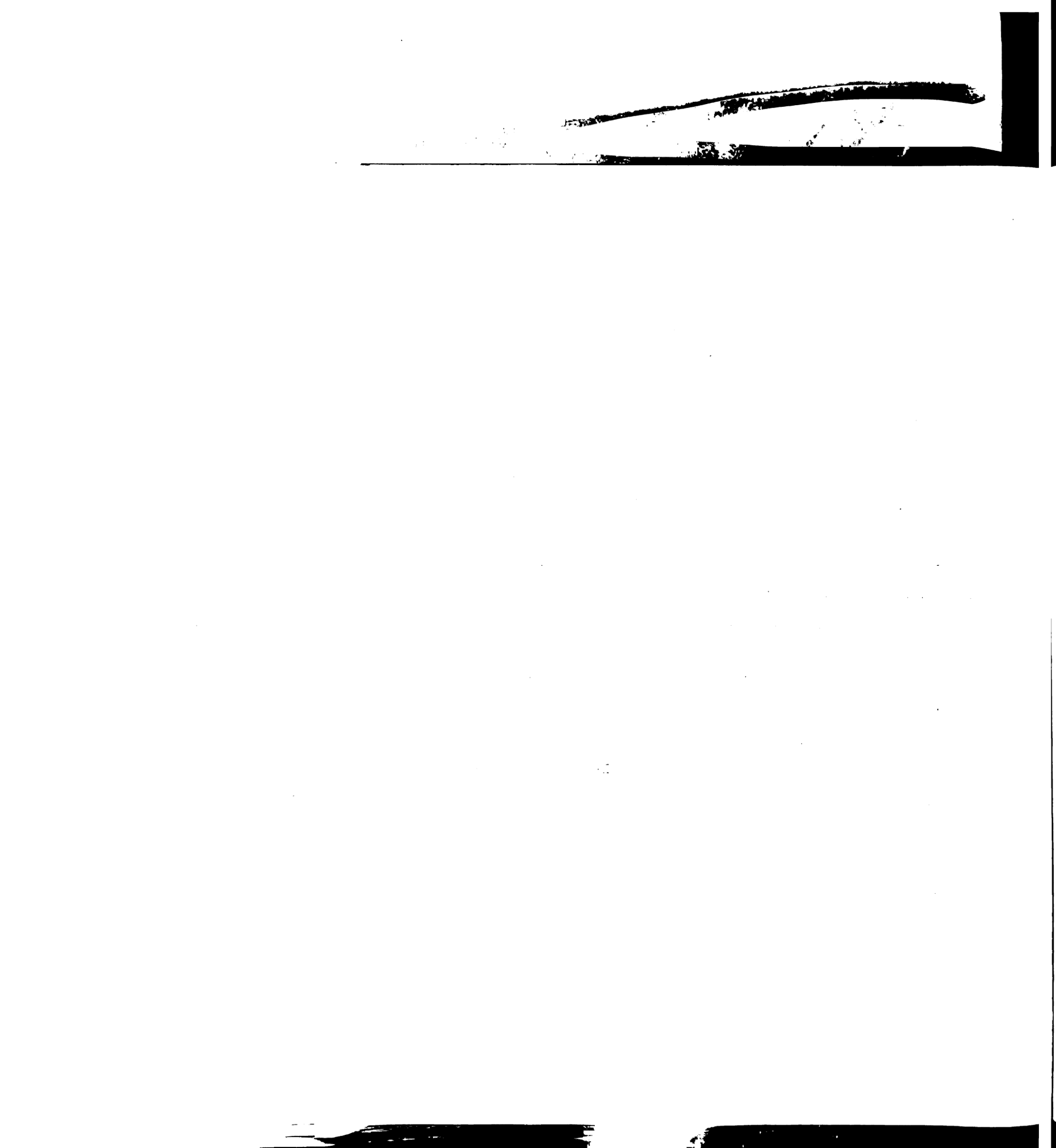
6 $C_6H_{11}OH$ + $(C_6H_{11}OBO)_3$ ⟶ 3 $(C_6H_{11}O)_3B$ + 3 H_2O,

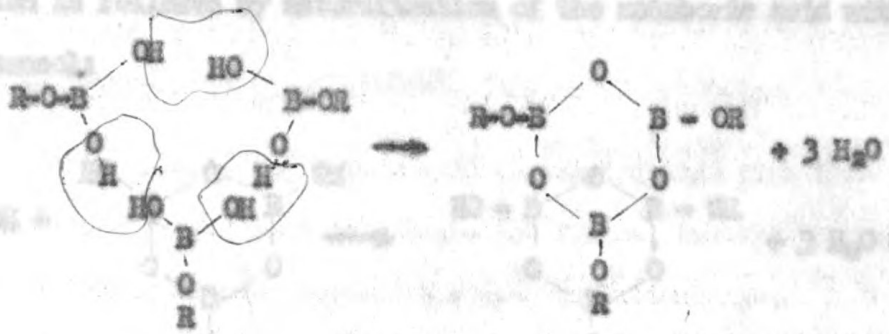
15.0 g. (0.150 mole) cyclohexanol was added to 9.5 g. (0.025 mole) tricyclohexoxyboroxine dissolved in 200 ml. of dry toluene. The mixture was refluxed using a constant water separator with stirring. After 3 hours the amount of water removed remained at 1.3 ml. (theoretical, 1.35 ml.). Stirring was stopped and the clear solution allowed to cool to room temperature; the solution remained clear. The majority of the toluene was removed by distillation and the flask was cooled to room temperature. A low-melting white solid resulted. The material was distilled at reduced pressure, the bulk of the material being collected at 195-198°/15 mm. The yield of $(C_6H_{11}O)_3B$ was 21 g. (91%). The white solid (m.p., 55-57° C.) was analyzed for boron: found, 3.58% B; calculated for $(C_6H_{11}O)_3B$, 3.51% B.

Discussion

O'Connor and Kuck (23) mention the alkoxyboric acid, $RB(OH)_2$, as a possible intermediate in the preparation of the metaborate ester, $(RBO)_3$, by esterification of orthoboric acid with l-menthol or cyclohexanol. If the alkoxyboric acid is an intermediate, the reaction would proceed as follows:

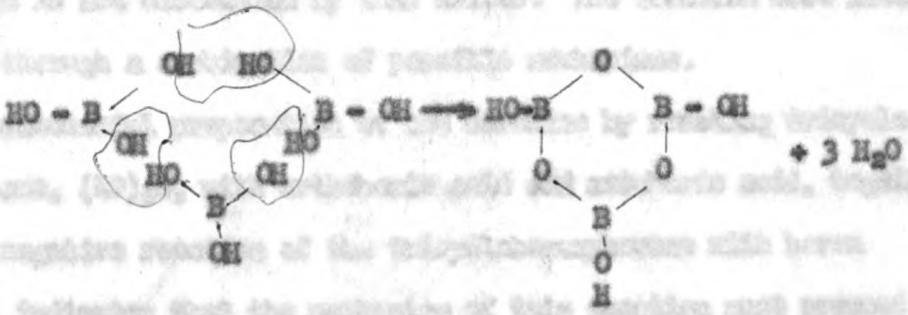
1. $ROH + B(OH)_3 \longrightarrow RB(OH)_2 + H_2O$



2. 

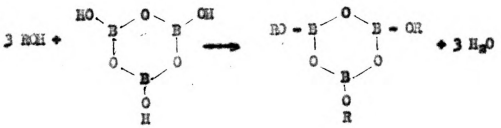
In an unsuccessful attempt to prepare the alkoxyboric acid (by stopping at step 1), O'Connor and Nace (23) used benzene as the inert solvent. These investigators stated that "benzene was used in place of toluene because boric acid does not lose water below 100°, and thus it might be possible to stop the reaction at the alkoxy acid stage." However, it was found in this thesis investigation (see Section III, page 60) that orthoboric acid is dehydrated to metaboric acid by refluxing in benzene.

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

3. 

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

4.



Evidence in support of this mechanism is 1) the fact that orthoboric acid is dehydrated to metaboric acid by refluxing in toluene or benzene, 2) metaboric acid is trimeric (65), 3) metaboric acid reacts with cyclohexanol to form tricyclohexoxyboroxine, and 4) cyclohexoxyboric acid has never been isolated.

In the case of the reaction of cyclohexanol with boron trioxide to form tricyclohexoxyboroxine, a possible mechanism is that the boron trioxide is partially hydrated to metaboric acid by initial esterification, and the metaboric acid thus formed is then esterified to form the boroxine.

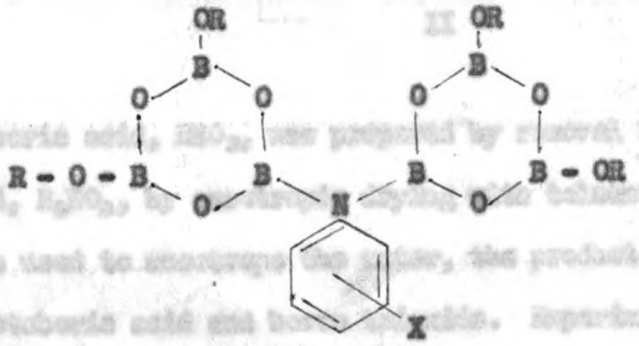
The possibility of the reaction proceeding through the alkoxyboric acid stage is not discounted by this writer. The reaction most likely proceeds through a combination of possible mechanisms.

The successful preparation of the boroxine by reacting tricyclohexoxyborane, $(RO)_3B$, with orthoboric acid and metaboric acid, together with the negative reaction of the tricyclohexoxyborane with boron trioxide, indicates that the mechanism of this reaction must proceed through the removal of water.

SUMMARY

The method of Goubeau and Keller (16) (boron trioxide plus trialkoxyborane, $(RO)_3B$) was used to prepare triethoxy-, tri-n-propoxy-, 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 30° C., the compounds prepared were liquids at room temperature. Of the boroxines studied, all decomposed upon attempted distillation to split off the corresponding trialkoxyborane. The densities of the boroxines studied increased with increased 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 $(ROBO)_3$.

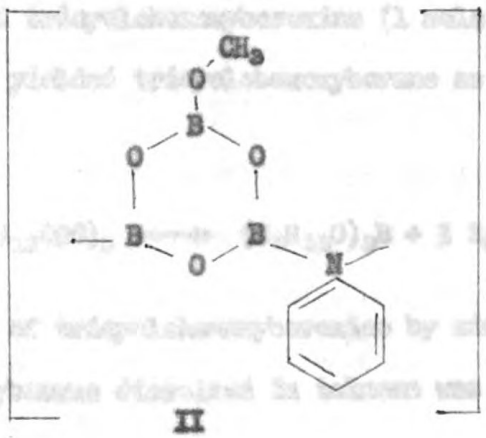
Addition of an ether solution of an aniline (aniline p-chloroaniline, p-anisidine, p-nitroaniline, p-aminobenzoic acid, p-toluidine, and p-aminoacetophenone) to an excess of trimethoxyboroxine in ether solution at room temperature produced a precipitate which can be represented by Structure I.



I

Triethoxyboroxine was also successfully used in the reaction, but tri-n-propoxy-, tri-n-butoxy-, tri-sec-butoxy-, triisobutoxy-, tri-n-pentoxy-, tri-n-octoxy-, and tri-n-dodecoxyboroxine yielded no visible reaction products under identical conditions. The products obtained from the reactions of the diamines, benzidine and phenylenediamine, with TMB and TEB are apparently mixtures containing both three and four dialkoxyboroxinyl groups attached to one molecule of diamine.

Gum-like polymers are produced from aniline and trimethoxyboroxine 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. The repeating unit in the polymer appears to have the structure II.



II

Metaboric acid, HBO_2, was prepared by removal of water from orthoboric acid, H_3BO_3, by azeotropic drying with toluene or benzene. When xylene was used to azeotrope the water, the product had a boron content between metaboric acid and boron trioxide. Experimental evidence that

the metaboric acid produced in both the benzene and toluene experiments is HBO_2III is the melting point (175° C.) and the density (1.78). X-ray powder diagrams and *d* values are given for orthoboric acid, metaboric acid, boron trioxide, and the xylene dehydration product of orthoboric acid. A comparison of the solubilities of orthoboric acid, metaboric acid, and boron trioxide in a series of aliphatic alcohols (methyl-, ethyl-, n-propyl-, n-butyl-, n-amyl-, and n-heptyl-) is given.

Tricyclohexoxyboroxine was prepared by reacting: 1) cyclohexanol with orthoboric acid, 2) cyclohexanol with metaboric acid, 3) cyclohexanol with boron trioxide, 4) tricyclohexoxyborane with orthoboric acid, and 5) tricyclohexoxyborane with metaboric acid. All of the above reactions were run in toluene with azeotropic removal of water. The reaction of cyclohexanol (6 moles) and tricyclohexoxyboroxine (1 mole) in toluene in stoichiometric amounts yielded tricyclohexoxyborane as indicated by the following reaction:

$$6\ C_6H_{11}OH + (C_6H_{11}OBO)_3 \longrightarrow (C_6H_{11}O)_3B + 3\ H_2O$$

The attempted preparation of tricyclohexoxyboroxine by addition of boron trioxide to tricyclohexoxyborane dissolved in toluene was unsuccessful.

FUTURE EXPERIMENTAL PROBLEMS

A number of alkoxyboroxines have been prepared and characterized in this investigation and that of Lappert (25). The only aryloxyboroxine reported, however, is triphenoxyboroxine, which was prepared by Lappert (25) by reacting triphenyl orthoborate with boron trioxide. It would seem probable that triphenoxyboroxine, and other aryloxyboroxines, could be prepared by reacting the appropriate phenol with orthoboric acid in toluene with constant removal of the water of esterification.

Although there are a few cases mentioned where alkylboroxines yield precipitates when reacted with ammonia, the only quantitative work reported is Burg's (26) reaction of trimethylboroxine with ammonia and methylamine. Thus the reactions of ammonia and amines with the boroxines, both $(RBO)_3$ and $(ROBO)_3$ should afford extensive research possibilities.

The use of such compounds as benzene, toluene, xylene, etc. for azeotropic removal of water from inorganic compounds has not received any attention 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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