[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

Boroxines. I. Alkyl Derivatives[1]

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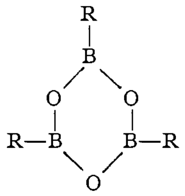
The properties of tri-*n*-butylboroxine, in particular, were examined. This compound, $(n\text{-BuBO})_3$, when refluxed in air-free water for several hours yields butane. In contrast to $B(n\text{-Bu})_3$, the boron–carbon bonds in $(n\text{-BuBO})_3$ are unaffected by chlorine; rather chlorine converts some of the *n*-butyl groups to *n*-butenyl groups, $CH_3CH_2CH{=}CH{-}$. Tri-*n*-butylboroxine, in the absence of oxygen and water, shows no appreciable decomposition below about 600° when passed slowly through a heated tube; above this temperature decomposition occurs with the production of >B–Et groups and ethylene. Treatment of tri-*n*-butylboroxine with aluminum chloride, phosphorus pentachloride or boron trichloride gives $B(n\text{-Bu})Cl_2$, while the interaction with trimethylaluminum, methylaluminum iodide or methylmagnesium iodide yields by an analogous reaction the trialkyl borane, $B(n\text{-Bu})Me_2$. This appears to be the first reported case of a mixed alkyl borane.

Introduction

Boroxines[2] are compounds in which boron and oxygen atoms alternate in a six-membered ring which is isoelectronic with and dimensionally similar to benzene



Alkyl, aryl, halo, alkoxy or amino groups may be bonded to the boron atoms. A structure determination[3] of trimethylboroxine by the electron diffraction technique indicates that the methyl groups are bonded to the boron atoms and that the carbon atoms are in the plane of the boron–oxygen ring. Boroxines, boric oxide, metaboric acid and the metaborates all have a common line (805 cm.$^{-1}$) in their Raman spectra; this line was attributed by Goubeau[4] to the ring as a whole. X-Ray analyses[5] also indicate that metaboric acid and the metaborates have the boroxine ring.

In spite of the fact that boroxines are not new compounds, their reported chemical properties are limited almost entirely to the observations that they are easily oxidized and hydrated.[4,6–9] Our original interest in these compounds stemmed from the report[7] that trichloroboroxine in particular appears to dissolve boric oxide; however, this boroxine is stable only above 200°. Tri-*n*-butylboroxine is considerably more stable than trichloroboroxine but dissolves only a small amount of boric oxide. In the course of attempting chlorination reactions on suspensions of boric oxide in $(n\text{-BuBO})_3$, interest shifted to the reactions of $(n\text{-BuBO})_3$ itself and other alkyl boroxines.

Experimental

Apparatus and Procedures

Vacuum System.—The vacuum system was constructed of Pyrex glass and all joints were lubricated with "Halocarbon Stopcock Grease" which is particularly unreactive toward all compounds used in this investigation and is readily soluble in a number of the common solvents such as acetone, methanol and ether. In addition to mercury as a manometer fluid, "Kel-F polymer oil" was used in certain instances. This oil was useful because it has a very low vapor pressure at room temperature and is unreactive toward all compounds met in this work. Its low density gave high accuracy in reading pressures below 25 mm.

Analyses.—Boron was determined by titrating a boric acid solution in the presence of mannitol with carbonate-free NaOH. The sample was first hydrolyzed with water or refluxed in a mixture of NaOH and 30% H_2O_2 for several hours.[6] Chloride was titrated with $AgNO_3$ and a Ag/AgCl electrode used to determine the endpoint potentiometrically. Nitrogen was determined by the Kjeldahl method.

Molecular weight determinations were made by the vapor density method using a 125-ml. bulb fitted with a stopcock and a male ball joint so that it could be attached to the vacuum system.

Vapor Pressure as a Function of Temperature.—For obtaining vapor pressures an isoteniscope was constructed so as to fit into a clear Dewar flask along with a thermometer, heating element and an air stirrer.

Infrared spectra were obtained with a Perkin–Elmer Model 12B spectrograph. The gas cell was filled on the vacuum system by the usual techniques. In order to get viscous compounds like $(n\text{-BuBO})_3$ into a 0.025 mm. liquid cell it was necessary to use nitrogen at about 25 pounds pressure to force them in. The cell was cleaned by blowing the compound out and rinsing the cell with absolute alcohol.

Preparation of Reagents

Aluminum bromide was prepared by a continuous process in which bromine vaporized in nitrogen was passed over aluminum turnings in a flask heated to about 300° and the resulting $AlBr_3$ then distilled over aluminum in a second flask to remove any unreacted bromine. The reaction of aluminum with bromine vapors is much smoother and easier to control than the reaction of aluminum with liquid bromine.

Boron tribromide was prepared by the method of Gamble, *et al.*,[10] but when this procedure was modified for use on a larger scale (500–1000 g. of $AlBr_3$) the yield was rather poor. A considerable saving of time resulted by passing bromine vaporized in a stream of BF_3 over heated aluminum turnings.

Boric Oxide.—Crystalline oxide was obtained by dehydrating boric acid in an Abderhalden vacuum drying chamber at a pressure of 1 mm. and a temperature of 265°.

Trimethoxyborane, $B(OCH_3)_3$.—(Modification of procedure of Schlesinger and co-workers).[11] It was found that

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[2] These compounds also have been called boroxoles, boronic anhydrides, triborine trioxanes and trimeric alkylboron oxides.

[3] S. H. Bauer and J. Y. Beach, THIS JOURNAL, **63**, 1394 (1941).

[4] J. Goubeau and H. Keller, *Z. anorg. allgem. Chem.*, **272**, 303 (1953).

[5] H. Tazaki, *J. Sci. Hiroshima Univ.*, **A10**, 55 (1940).

[6] H. R. Snyder, J. A. Kuck and J. R. Johnson, THIS JOURNAL, **60**, 105 (1938).

[7] J. Goubeau and H. Keller, *Z. anorg. allgem. Chem.*, **265**, 73 (1951).

[8] J. Goubeau and H. Keller, *ibid.*, **267**, 1 (1951).

[9] H. C. Mattraw, C. E. Erickson and A. W. Laubengayer, THIS JOURNAL, **78**, 4901 (1956).

[10] E. Lee Gamble, P. Gilmont and J. F. Stiff, *ibid.*, **62**, 1257 (1940).

[11] H. I. Schlesinger, H. C. Brown, D. L. Mayfield and J. R. Gilbreath, *ibid.*, **75**, 213 (1953).

more $B(OCH_3)_3$ could be obtained in less time by omitting the sulfuric acid and by first collecting methanol–trimethoxyborane fractions and distilling the azeotrope from the combined fractions rather than distilling directly from the methanol and boric acid mixture. The $B(OCH_3)_3$ was separated from the azeotrope by refluxing the latter over anhydrous LiCl in the usual way.[11]

***n*-Butyldihydroxyborane, $B(n\text{-}Bu)(OH)_2$**, was prepared by the method of Snyder and co-workers.[6] The white, waxy crystals obtained in this way were formerly thought[6] to be the monohydrate, but more recently a claim[9] has been made that these crystals are anhydrous.

Tri-*n*-butylboroxine, $(n\text{-}BuBO)_3$.—This reagent was prepared in a small distillation assembly which was connected to the vacuum system at the receiver end. Solid $B(n\text{-}Bu)(OH)_2$ was placed in the distilling flask and a high vacuum applied. After all the absorbed petroleum ether and water had been removed, as evidenced by a lowering of the pressure in the system, the solid was warmed slightly until only liquid was present. It was necessary to exercise caution in this operation because sublimation occurred and the condenser became plugged when the heating was carried out too rapidly. The rate of heating was increased until $(n\text{-}BuBO)_3$ distilled into the receiving flask. A yield of 97% was obtained by this method instead of 50% as reported by Snyder and co-workers.[6] The following relationship was found for this compound in the pressure range 1 to 30 mm.: $\log p(\text{mm.}) = -4550/T + 12.34$. This compound is a colorless liquid with a reported[9] b.p. of 259°.

Anal. Calcd. for $B_3C_{12}H_{27}O_3$: B, 13.1. Found: B, 12.91.

Methylaluminum Iodide.—This substance was prepared directly from methyl iodide and aluminum turnings without a solvent.[12]

Trimethylaluminum was prepared in a manner similar to that used for methylaluminum iodide except that the product was distilled from the reaction flask in the presence of 10 to 20 mm. of nitrogen. The nitrogen raised the temperature sufficiently so that methylaluminum iodide disproportionated to give trimethylaluminum as one product.[13]

Methylmagnesium Iodide.—This compound was prepared from magnesium and methyl iodide in dibutoxytetraethylene glycol as a solvent. This glycol was used because of its high boiling point, since the solution of methylmagnesium iodide was to be used in a subsequent reaction in which a volatile solvent would be undesirable. The preparation of the Grignard reagent in this glycol proceeded quite satisfactorily although the resulting solution was extremely viscous and foamed quite badly.

Trimethylborane.—A 35-ml. 3-necked flask was fitted with a stopper, a Liebig condenser packed with helices, and an inverted U-tube fitted with a bulb. Methylmagnesium iodide (0.3 mole) in *n*-butyl ether was placed in the reaction flask and $B(OCH_3)_3$ (0.1 mole) was placed in the bulb. The condenser was cooled by a circulating mixture of Dry Ice and acetone and its top was attached to a receiving flask *via* the vacuum system. The bulb and reaction flask were immersed in Dry Ice–acetone baths while the apparatus was evacuated. The cooling baths were then removed and the receiving flask was immersed in a liquid nitrogen bath. By temperature control of the bulb containing the $B(OCH_3)_3$, this compound was permitted to diffuse slowly into the reaction zone. With the reactants stirred by a magnetic stirrer, BMe_3 was collected in the receiving flask.

Anal. Calcd. for BC_3H_9: mol. wt., 55.8. Found: mol. wt., 55.

***n*-Butylmagnesium bromide** was prepared in large amounts, standardized and used as needed.

Ethyldihydroxyborane, $BEt(OH)_2$, was prepared from $B(OCH_3)_3$ in dry ethyl ether and ethylmagnesium bromide in a manner analogous to that used for $B(n\text{-}Bu)(OH)_2$. In this case, however, the distillation of the ether layer was cut short because the boron product was being carried over. The crystals obtained by chilling the ether solution were purified by sublimation.

Isobutyldihydroxyborane, $B(iso\text{-}Bu)(OH)_2$, was obtained by the interaction of isobutylmagnesium bromide with $B(OCH_3)_3$ in dry ether as outlined above for $B(n\text{-}Bu)(OH)_2$.

Triisobutylboroxine, $(iso\text{-}BuBO)_3$.—Purified crystals of $B(iso\text{-}Bu)(OH)_2$ were placed in a flask cooled in a Dry Ice–acetone mixture. After these crystals had been under a vacuum for one hour, they were heated gently. However, instead of dehydrating to give $(iso\text{-}BuBO)_3$, the crystals decomposed with the formation of boric oxide and unidentified products.

Crude crystals of $B(iso\text{-}Bu)(OH)_2$ were then washed with 9 *N* H_2SO_4 and dissolved in ether. Crystals of $B(iso\text{-}Bu)(OH)_2$ were again obtained by processing the ether solution according to the method of Snyder and co-workers[6] for $B(n\text{-}Bu)(OH)_2$. The dehydration of solid $B(iso\text{-}Bu)(OH)_2$ obtained in this manner proceeded smoothly to give $(iso\text{-}BuBO)_3$. At present we have no satisfactory explanation for this phenomenon. Properties were n^{20}_D 1.4118; d^{24}_4 0.865.

Anal. Calcd. for $B_3C_{12}H_{27}O_3$: B, 13.1. Found: B, 12.8 and 13.1.

The following relationship was found for this compound between 260 microns and 30 mm.: $\log p(\text{mm.}) = -5250/T + 13.98$.

Attempted Preparation of $(EtBO)_3$.—Because of a marked tendency for $BEt(OH)_2$ to sublime, this substance could not be dehydrated to $(EtBO)_3$ by being heated under a vacuum. When warmed in contact with thionyl chloride, acetyl chloride or benzoyl chloride, $BEt(OH)_2$ sublimed out of contact with each of these reagents. When placed at the bottom of a column of $CaSO_4$ and the column evacuated, the $BEt(OH)_2$ sublimed through the column into the vacuum system.

Boron-10 Trifluoride.—The trifluoride of boron containing 80% boron-10 was prepared by heating a boron trifluoride–calcium fluoride complex *in vacuo*. The complex was obtained from the Atomic Energy Commission, Oak Ridge, Tenn.

Boron-10 tribromide[14] was prepared by the interaction of $B^{10}F_3$ with $AlBr_3$ according to the method of Gamble, *et al.*[10] The $B^{10}Br_3$ was purified by distillation in a nitrogen atmosphere.

Reactions and Properties

Reaction of $(n\text{-}BuBO)_3$ with Halides to Form $B(n\text{-}Bu)Cl_2$.—Tri-*n*-butylboroxine (5 ml.) was added dropwise to 5 g. of $AlCl_3$ under reduced pressure (less 50 μ) at room temperature. A volatile material collected in a receiver cooled in liquid nitrogen while a tarry residue remained in the reaction flask. When the receiver and contents were warmed to Dry Ice temperature HCl escaped and $B(n\text{-}Bu)Cl_2$ remained as a colorless liquid.

Anal. Calcd. for $BC_4H_9Cl_2$: B, 7.75; mol. wt., 139. Found: B, 7.7; mol. wt., 138–139.

A log *p vs.* 1/*T* curve when extrapolated to 760 mm. indicated a b.p. of 109° for the compound. The literature value[15] is 107.9°.

An analogous reaction occurred between $(n\text{-}BuBO)_3$ and BCl_3 or PCl_5, but no indication of a reaction was observed with $AsCl_3$, $SbCl_5$, $ZnCl_2$, $HgCl_2$ and $CaCl_2$. The attempted reaction with anhydrous $CaCl_2$ was carried out under a variety of conditions, including heating these substances in a hot tube and a pressure bomb, but no evidence of a reaction was obtained.

Formation of $B(n\text{-}Bu)Me_2$ from $(n\text{-}BuBO)_3$.—Methylaluminum iodide (5 ml.) was added slowly from a dropping funnel to 5 ml. of $(n\text{-}BuBO)_3$ in an evacuated reaction flask attached to the vacuum system. An exceedingly violent reaction took place, occasionally accompanied by incandescence, and a volatile material collected in the receiving flask. At the cessation of the reaction, the reaction flask was warmed for 10 minutes. Then the material in the receiving flask was fractionated, the $B(n\text{-}Bu)Me_2$ being collected as the fraction having between 80 and 90 mm. of vapor pressure at room temperature. Trimethylaluminum can be substituted for methylaluminum iodide in this procedure with no change in the results. $B(n\text{-}Bu)Me_2$ was also prepared by the interaction of $(n\text{-}BuBO)_3$ with methylmagnesium iodide in dibutoxytetraethylene glycol as solvent. Because of the high boiling point of this glycol, the reaction product was obtained free of solvent.

Anal. Calcd. for BC_6H_{15}: B, 11.1; mol. wt., 98. Found: B, 11.5 and 11.4; mol. wt., 100 and 102.

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(12) A. V. Grosse and J. M. Mavity, *J. Org. Chem.*, **5**, 106 (1940).

(13) K. S. Pitzer and H. S. Gutowsky, THIS JOURNAL, **68**, 2204 (1946).

(14) We are indebted to Eugene M. Vander Wall of our laboratory for this preparation.

(15) R. B. Booth and C. A. Kraus, THIS JOURNAL, **74**, 1415 (1952).

$B(n\text{-Bu})_2Me$.—When the etherate of trimethylaluminum was allowed to react with $(n\text{-BuBO})_3$, in addition to $B(n\text{-Bu})Me_2$ a trace of material was obtained whose molecular weight agreed with $B(n\text{-Bu})_2Me$. This compound is a possible disproportionation product of $B(n\text{-Bu})Me_2$. While there was not enough of this material to analyze, its infrared spectrum was determined and the most intense absorption peaks were found to be at 7.65, 8.10 and 8.77 μ.

Action of Chlorine on $(n\text{-BuBO})_3$.—$(n\text{-BuBO})_3$ was refluxed in oxygen-free chlorine for 5 minutes, the HCl and residual chlorine removed from the reaction flask, more chlorine added and the cycle repeated until there was no indication of a reaction upon the addition of more chlorine. In the course of these reaction cycles, the amount of HCl formed agreed with the quantity of chlorine consumed. A deep-red liquid resulted which decomposed when distilled under high vacuum. An analysis of the crude liquid indicated that the percentage boron corresponded within experimental error to that for pure $(n\text{-BuBO})_3$; a trace of chlorine was found which could be due to a slight amount of dissolved HCl.

Three milliliters of the above liquid was mixed with 5 ml. of 30% H_2O_2. A white amorphous solid appeared which dissolved upon the addition of a few drops of 1 *N* NaOH. After gently warming this basic solution for a few moments, ether was added to the water layer saturated with NaCl. The ether layer was separated and added to a solution of 2,4-dinitrophenylhydrazine in alcohol and H_2SO_4. After standing overnight the mixture deposited crystals.

Anal. Lit. value[16] for 2,4-dinitrophenylhydrazone of *n*-butyraldehyde: m.p. 122°. Found: m.p. 120–121°.

Effect of Heat on $(n\text{-BuBO})_3$.—The pyrolysis apparatus consisted of a 1-inch "Vycor" tube wrapped with layers of asbestos and nichrome wire and fitted with a dropping funnel and a receiving flask. Since the apparatus was made an integral part of the vacuum system, reactions could be run in the complete absence of air. The reaction tube had a very sharp temperature gradient; the temperature rose from room temperature to the reaction zone temperature in about two inches of tube length. The high temperature zone was uniform for the central twelve inches of the reaction tube. During the pyrolysis reactions the pressure beyond the tube was maintained at approximately 100 μ.

$(n\text{-BuBO})_3$ was allowed to drop slowly from the addition funnel into the tube. Upon striking the tube the liquid flowed downward until it was heated sufficiently to vaporize. At 600° the liquid which collected in the receiving flask was unchanged $(n\text{-BuBO})_3$. At 750° a liquid again collected in the receiving flask, but in addition a more volatile material collected in a cold trap beyond the receiving flask. The latter material was identified by means of infrared, vapor pressure and molecular weight measurements as ethylene with a trace of higher hydrocarbons. The material in the first receiving flask when treated with $AlCl_3$ produced predominantly $BEtCl_2$.

Anal. Calcd. for $BC_2H_5Cl_2$: B, 9.92; Cl, 64; mol. wt., 111. Found: B, 10.35; Cl, 59; mol. wt., 108–114.

Effect of Water on $(n\text{-BuBO})_3$.—This compound was refluxed in oxygen-free water for two hours during which time the pressure in the system gradually increased. The volatile product was collected in a trap immersed in liquid nitrogen and was shown by vapor pressure and infrared measurements to be butane. An amount of butane equivalent to approximately 10% of the starting boroxine was obtained.

Triisobutylboroxine.—The presence of an isobutyl group attached to boron was confirmed in the following way. Three milliliters of $(iso\text{-BuBO})_3$ was added to 10 ml. of 30% H_2O_2. When the reaction had ceased, ether was added and the water layer was saturated with NaCl. The ether layer was separated and added to 3,5-dinitrobenzoyl chloride; water was added and the crystals which formed were removed. After recrystallization from aqueous ethanol, the m.p. of this derivative was found to be 84–85°. The literature value[16] for isobutyl 2,5-dinitrobenzoate is 86°.

Reaction of $AlCl_3$ with $(iso\text{-BuBO})_3$.—Three milliliters of $(iso\text{-BuBO})_3$ was distilled onto 5 g. of $AlCl_3$ in a reaction flask cooled by liquid nitrogen. This bath was removed and a clear colorless liquid collected in a receiving flask cooled by liquid nitrogen. A one-plate distillation gave a volatile fraction and left a deep-red waxy substance in the distilling flask. The volatile material was separated into two parts: one was BCl_3 with a trace of isobutane and the other isobutane as determined by molecular weight and infrared measurements. Infrared analysis also showed a trace of material that was unsaturated, but its amount was much less than that of the isobutane.

Reaction of *n*-Butenylboroxine[20] with $AlCl_3$.—The addition of *n*-butenylboroxine (3 ml.) dropwise to 5 g. of $AlCl_3$ caused a very violent reaction to take place. The inside of the system became covered with a red tarry material and a clear colorless liquid collected in a receiving flask cooled by liquid nitrogen. Repeated attempts were made to characterize the colorless liquid, but the material was unstable at room temperature. Since this substance had only 20–30 mm. of vapor pressure at room temperature it was not practical to work with it at lower temperatures.

Two definite mixtures of compounds could be isolated from the above reaction products, but further characterization of these mixtures could not be achieved. The first mixture had a molecular weight of 100–115, did not give any visible reaction on exposure to air, had 24–27 mm. of vapor pressure at room temperature, and had two chlorine atoms for each boron atom. However, the mixture evidently contained some molecules which were boron-free. The other mixture of compounds had a molecular weight of 200–250, was spontaneously explosive on contact with air, had an average composition of two boron atoms and three chlorine atoms per molecule, and a vapor pressure of 20–25 mm. at room temperature.

Addition Complexes of $B(n\text{-Bu})Me_2$.—Four milliliters of $B(n\text{-Bu})Me_2$ was frozen into excess pyridine. When the reactants had warmed up to room temperature, air was admitted, excess pyridine was removed by distillation, and a clear colorless liquid was then collected upon gentle heating of the distilling flask. This liquid began to discolor in air, going slowly from light yellow to dark brown. Analytical and infrared data indicated that in the distillation the $B(n\text{-Bu})Me_2$ had disproportionated; the product collected was $BMe_3\cdot$pyridine[17] with a slight amount of excess pyridine.

The above procedure was repeated except that an attempt was made to obtain the pyridine adduct by extracting the reaction mixture with petroleum ether. The petroleum ether extracts were placed over $CaSO_4$ for 24 hours. After filtration and evaporation of the petroleum ether, a colorless liquid remained which proved to be $B(n\text{-Bu})Me_2\cdot$pyridine contaminated with a slight amount of pyridine.

Anal. Calcd. for $BC_{11}H_{19}N$: B, 6.12; N, 7.92. Found: B, 5.80; N, 8.13.

No adducts could be isolated from reaction mixtures of $B(n\text{-Bu})Me_2$ with NH_3, NMe_3, β-naphthylamine, benzonitrile and quinoline. In the case of NH_3 and NMe_3 colorless viscous liquids were obtained but these were not investigated further.

Reaction of Methylating Agents with B_2O_3.—Boric acid which had been heated in a vacuum dryer using ethyl phthalate as the refluxing liquid was crushed to a fine powder and placed in a small flask. The flask was evacuated and then heated with a gas flame until the oxide just started to soften. The boric oxide was removed and re-crushed. The cycle was repeated three times. Two milliliters of trimethylaluminum was frozen onto 5 g. of this oxide by means of liquid nitrogen and the mixture then gently heated for four hours. The infrared spectrum of the material collected in a liquid nitrogen-cooled receiver was identical with that of BMe_3. The same results were obtained with trimethylaluminum iodide and boric oxide. The yields in these reactions were poor principally because the surface of the boric oxide became coated as the products were formed.

Miscellaneous Reactions.—$(n\text{-BuBO})_3$ was refluxed over crystalline boric oxide at a pressure of less than 100 μ. The crystalline boric oxide disappeared from the bottom of the reaction flask and a glassy material appeared as a ring around the flask immediately above the liquid. The liquid in the flask following this reaction contained, within experimental error, the same amount of boron as pure $(n\text{-BuBO})_3$. Apparently the boric oxide dissolved and was then deposited on the upper and cooler walls of the flask. No determination of the solubility could be made however.

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(16) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 229.

(17) H. C. Brown and J. D. Brady, THIS JOURNAL, **74**, 3570 (1952).

Methylaluminum iodide was refluxed for 4 hours with crushed dry sodium metaborate. There was no indication of a reaction in spite of the fact that the metaborates presumably have a boroxine ring structure.[4,5]

Tri-*n*-butylboroxine was added dropwise to $LiAlH_4$ in dry dibutoxytetraethylene glycol and the resulting mixture stirred for two hours. Then the mixture was refluxed (about 150°) for one-half hour. Hydrogen was produced by the decomposition of $LiAlH_4$ and an extremely small amount of another volatile material was collected; the latter, however, was boron-free. Sodium hydride produced the same volatile material. The identity of this substance was not established.

When BMe_3 containing normal isotopic boron and BBr_3 enriched in boron-10 were placed together in an infrared gas cell with NaCl windows, an exchange of boron atoms took place; simultaneous with this exchange there appeared a boron–chlorine absorption peak in the infrared spectrum. However, if the gas cell had recently been exposed to BBr_3, no exchange took place. These facts suggest that exchange takes place between NaCl and BBr_3 to form BCl_3; it may then be the BCl_3 which actually exchanges with the BMe_3.

Discussion of Results

Tri-*n*-butylboroxine.—This compound is unaffected by oxygen in the absence of water but is oxidized in the presence of water. It was shown in the present work that when this boroxine is refluxed in oxygen-free water, butane is slowly produced. Inasmuch as the primary reaction of $(n\text{-BuBO})_3$ with water should yield $B(n\text{-Bu})(OH)_2$, it may be that the butane results from the interaction of water with the latter compound and not from tri-*n*-butylboroxine itself.

Reaction of $(n\text{-BuBO})_3$ with Halides.—Aluminum chloride reacts vigorously under vacuum below room temperature with $(n\text{-BuBO})_3$ to produce water-white $B(n\text{-Bu})Cl_2$, a tarry residue and some HCl. The formation of $B(n\text{-Bu})Cl_2$ is very nearly quantitative when the boroxine is in excess and the yields are calculated on the basis of the aluminum chloride. If the aluminum chloride is in excess, it becomes very difficult to remove all the volatile materials from the products. While a similar reaction occurs with PCl_5, neither $SiCl_4$ nor $TiCl_4$ appears to react. This suggested that "Lewis acids" are necessary for such a reaction. Accordingly, $(n\text{-BuBO})_3$ was treated with BCl_3, $SbCl_5$, $AsCl_3$ and $HgCl_2$ all of which are Lewis acids and with $CaCl_2$ which is not a Lewis acid. Boron trichloride was the only one of these halides that was found to react; the reaction product was also $B(n\text{-Bu})Cl_2$.

The small amount of HCl in these reactions may have arisen from traces of water in the reactants or, since a tarry residue also was obtained, from a more complicated reaction.

Formation and Properties of $B(n\text{-Bu})Me_2$.—If trimethylaluminum were to react with $(n\text{-BuBO})_3$ analogous to the way in which $AlCl_3$ reacts, the mixed alkyl borane, $B(n\text{-Bu})Me_2$, would be formed. Thus, the boroxines would offer new synthetic routes to boron derivatives. This reaction was attempted and, as anticipated, $B(n\text{-Bu})Me_2$ was obtained. Either trimethylaluminum or methylaluminum iodide (probably as a mixture of $AlMeI_2$ and $AlMe_2I$) was found satisfactory for this reaction. Since the methylaluminum iodide is considerably safer to use than trimethylaluminum, the former compound is preferred. A similar reaction to produce $B(n\text{-Bu})Me_2$ occurs between methylmagnesium iodide and $(n\text{-BuBO})_3$. If the boroxine is in excess in these reactions, a solution is present at the conclusion of the reaction; the volatile product can be removed cleanly from this solution. Under these conditions, the formation of $B(n\text{-Bu})Me_2$ is essentially quantitative in terms of the methylating agent.

$B(n\text{-Bu})Me_2$ is a water-white liquid, is spontaneously inflammable in air, and its vapor pressure obeys the relationship: $\log p(\text{mm.}) = -1750/T + 7.91$. Its infrared spectrum was found to have points of similarity with the spectra of BMe_3 and $B(n\text{-Bu})_3$, with the most intense absorption peaks being at 7.20, 7.70 and 8.77 μ.

$B(n\text{-Bu})Me_2$ does not react with water although water seems to aid its slow disproportionation into BMe_3 and $B(n\text{-Bu})_3$, and it evolves BMe_3 on contact with dilute acids. While $B(n\text{-Bu})Me_2$ is stable to 100° if pure, in the presence of pyridine it disproportionates forming the pyridine adduct of BMe_3 and presumably also of $B(n\text{-Bu})_3$. Upon treatment of the pyridine adduct of $B(n\text{-Bu})Me_3$ with dilute acids, BMe_3 is evolved immediately, and with water BMe_3 is evolved slowly. These facts strongly suggest that a donor molecule is necessary for the disproportionation to take place. If boron forms a fourth bond to a donor molecule, the other three bonds can be weakened making it easier for a transfer of alkyl groups to occur. Further support for the hypothesis that a donor molecule is necessary for the disproportionation to take place comes from a consideration of the conditions producing $B(n\text{-Bu})_2Me$, an intermediate disproportionation product of $B(n\text{-Bu})Me_2$. When trimethylaluminum was allowed to react with $(n\text{-BuBO})_3$ without a solvent, the only volatile product ever obtained was $B(n\text{-Bu})Me_2$. When ether (a donor molecule) was used as a solvent not only $B(n\text{-Bu})Me_2$ but also BMe_3 and $B(n\text{-Bu})_2Me$ were isolated as volatile products.

No satisfactory solid derivatives for characterizing $B(n\text{-Bu})Me_2$ were obtained with pyridine, ammonia, trimethylamine, β-naphthylamine, benzonitrile and quinoline. However, a fairly pure liquid adduct with pyridine, $B(n\text{-Bu})Me_2\cdot$pyridine, was prepared. Without a definitive derivative of $B(n\text{-Bu})Me_2$ it can be argued that molecular weight and analytical data would not distinguish between $B(n\text{-Bu})Me_2$ as such and a mixture containing a 1:2 molar ratio of $B(n\text{-Bu})_3$ and BMe_3. However, the latter situation appears extremely unlikely in view of the consistency with which the substance agreeing with the formula $B(n\text{-Bu})Me_2$ is obtained by different methods. Vapor pressure considerations also exclude a mixture as a possibility. The substance BMe_3 has a boiling point of −20° and $B(n\text{-Bu})_3$ has a vapor pressure of only about 30 μ at room temperature. The vapor pressure of $B(n\text{-Bu})Me_2$, on the other hand, is approximately 90 mm. at room temperature.

Reaction of $(n\text{-BuBO})_3$ with Chlorine.—When $(n\text{-BuBO})_3$ is refluxed in chlorine, HCl is evolved but no volatile product containing boron–chlorine bonds is formed as judged from infrared analyses. If the boron–carbon link in $(n\text{-BuBO})_3$ were cleaved by the chlorine, trichloroboroxine would be the expected product; this in turn would disproportionate to BCl_3 and boric oxide.[7] The evolution of HCl implies that the chlorine attacked the side chains. However, only a trace of chlorine was found in the product and its boron content was essentially the same as that in pure $(n\text{-BuBO})_3$. The crude liquid from this reaction when treated with $AlCl_3$ reacts violently to give a red tarry material and a clear colorless liquid stable at liquid nitrogen temperature but unstable at room temperature. There is no evidence whatsoever of $B(n\text{-Bu})Cl_2$, the product which would have formed had there been any unchanged $(n\text{-BuBO})_3$ present. The above analyses and the formation of HCl during the reaction can be explained if some of the *n*-butyl groups have been changed to *n*-butenyl groups, $CH_3CH_2CH{=}CH{-}$.

Direct proof that a double bond is present in the product resulting from the chlorination of $(n\text{-BuBO})_3$ is difficult to obtain;[18] consequently evidence for the double bond was secured indirectly. Tri-*n*-butylboroxine on treatment with basic peroxide yields *n*-butyl alcohol; this is a test for a $>$B–C–C– linkage. On the other hand isobutenyldihydroxyborane, $(CH_3)_2C{=}CH{-}B(OH)_2$, on treatment with neutral hydrogen peroxide gives isobutyraldehyde;[19] this is a test for a $>$B–C=C— linkage. When *n*-butenylboroxine[20] is treated with neutral hydrogen peroxide, *n*-butyraldehyde is formed in good yield.

Pyrolysis of $(n\text{-BuBO})_3$.—The pyrolysis experiments were designed to test the effect of heat on $(n\text{-BuBO})_3$ with as little interference from degradation products as possible. Accordingly, vapors of the boroxine were passed slowly through a heated tube under reduced pressure as opposed to heating the confined material in a bomb. Under these conditions $(n\text{-BuBO})_3$ was unaffected up to about 600° but at 750° was degraded to two fractions, one liquid at room temperature and the other gaseous. Since the volatile material was shown to be ethylene with a trace of higher hydrocarbons, the non-volatile material could contain $>B{-}CH_2CH_3$ groups. This latter liquid, which was nearly equal in volume to the starting $(n\text{-BuBO})_3$ sample, was too high boiling to permit effective purification by distillation; thus it was allowed to react directly with $AlCl_3$. The $AlCl_3$ converted the non-volatile material to a volatile material, which was fractionated into two portions. One portion (about 75% of the total) agreed in molecular weight and analysis with that of $BEtCl_2$ and the remaining portion showed a molecular weight between that for propyldichloroborane and butyldichloroborane. The infrared spectrum of the fraction in greater abundance agreed with the spectrum of a sample of $BEtCl_2$ prepared by the interaction of $BEt(OH)_2$ and $AlCl_3$. The second fraction was not completely characterized but appeared to be mainly a mixture of $BEtCl_2$ and $B(n\text{-Bu})Cl_2$.

These results point up the interesting fact that the boron–carbon bonds in $(n\text{-BuBO})_3$ are less subject to cleavage by pyrolysis than the carbon–carbon bonds in this molecule. From these data it is not possible to state unequivocally that $(n\text{-BuBO})_3$ molecules have been converted to $(EtBO)_3$ molecules, but it is highly probable that this is the case. In the products resulting from the aluminum chloride treatment of the non-volatile degradation material, the ratio of $BEtCl_2$ to $B(n\text{-Bu})Cl_2$ is more than 3 to 1. This implies either a mixture containing predominantly $(EtBO)_3$ with some $(n\text{-BuBO})_3$, or a mixture containing compounds with *n*-butyl and ethyl groups in the same molecule. It is probable that if a $(n\text{-BuBO})_3$ molecule is sufficiently energized so that a carbon–carbon bond in one butyl group is broken, the other two butyl groups will split also.

Other Boroxines.—A comparison of the properties of other alkyl boroxines with those of $(n\text{-BuBO})_3$ would be of fundamental interest. A start in this direction was made by preparing $(iso\text{-BuBO})_3$ and treating this substance with $AlCl_3$. However the expected product, $B(iso\text{-Bu})Cl_2$, was not obtained; rather isobutane and BCl_3 were isolated from the reaction products.

The compound $(EtBO)_3$ could not be obtained by dehydration of $BEt(OH)_2$ because of the great tendency of the latter compound to sublime. However, direct treatment of $BEt(OH)_2$ with $AlCl_3$ yielded $BEtCl_2$. The $(EtBO)_3$ produced when $(n\text{-BuBO})_3$ was pyrolyzed as mentioned above formed $BEtCl_2$ when treated with $AlCl_3$.

n-Butenylboroxine[20] obtained by the reaction of chlorine on $(n\text{-BuBO})_3$ gave a red tarry material and a clear colorless liquid when treated with $AlCl_3$. The clear colorless liquid was unstable, however, at room temperature. If *n*-butenyldichloroborane formed, it might be unstable because of a tendency to disproportionate.

Fajans and Barber[21] have suggested that boric oxide at low temperature consists of an array of discrete B_4O_6 units, each unit having four distorted boroxine rings for faces. The boron atoms are at the corners of a tetrahedron with one oxygen atom between each pair of boron atoms. Since the first step of the reaction of trimethylaluminum with $(n\text{-BuBO})_3$ probably involves a π-complex between the π-electrons on the boroxine ring and the empty orbital on the aluminum, it would be anticipated that this same type of reaction should occur when trimethylaluminum and boric oxide react. When trimethylaluminum or methylaluminum iodide was allowed to react with boric oxide the product obtained was BMe_3.

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[18] John C. Perrine, Ph.D. Thesis, University of Colorado, Boulder, Colorado, 1956.

[19] R. L. Letsinger and I. H. Skoog, *J. Org. Chem.*, **18**, 895 (1953).

[20] The general term "*n*-butenylboroxine" is used here because it is not known whether only one or two, or all three, of the *n*-butyl groups in any given molecule of $(n\text{-BuBO})_3$ have been converted to *n*-butenyl groups.

[21] K. Fajans and S. W. Barber, THIS JOURNAL, **74**, 2761 (1952).