by shaking intermittently over a period of ten hours with a solution of 5.5 g. of mercuric chloride and 10 g. of sodium acetate crystals in 80 cc. of water. The crude 2-chloromercurithiophene weighed 4.5 g. and melted at 179–180°. Recrystallization from acetone gave 4.0 g. of the pure mercury compound melting sharply at 181–182° (uncorr.).

In a similar experiment using ammoniacal silver nitrate solution, the original precipitate was white but changed to yellow on warming and then dissolved completely. From 2.3 g. of the boronic acid, 1.4 g. of thiophene was obtained (95% of the theoretical).

Replacement Reactions. (a) **Mercuric Chloride.**—When 2-thiopheneboronic acid was treated with a cold 6% aqueous solution of mercuric chloride a white precipitate formed immediately. This was recrystallized from alcohol, and finally from acetone, to give pure white crystals of 2-chloromercurithiophene, m. p. 181–182° (uncorr.).

(b) **Cupric Bromide.**—A solution of 2.3 g. of the boronic acid in 10 cc. of water was treated with 4 g. of cupric bromide. The blue color faded rapidly and a white precipitate of cuprous bromide appeared at once. By steam distillation 2.9 g. of 2-bromothiophene was obtained (practically quantitative yield), which was identified by mercuration in the usual way. The resulting 5-bromo-2-chloromercurithiophene was crystallized successively from alcohol and acetone, and found to melt at 222° (uncorr.), in agreement with the reported melting point.

(c) **Iodine and Bromine.**—Treatment of 2-thiopheneboronic acid with iodine in aqueous potassium iodide, or with iodine in the presence of dilute alkali, yields 2-iodothiophene. Similarly, the boronic acid decolorizes bromine water, but it does not decolorize bromine in carbon tetrachloride solution.

Summary

2-Furan- and 2-thiopheneboronic acids have been prepared. In their chemical behavior these acids show a marked resemblance to the aromatic boronic acids.

Aliphatic boronic acids containing the benzyl and *t*-butyl groups have been examined and were found to differ sharply in chemical behavior from the aromatic boronic acids. Both acids are quite susceptible to atmospheric oxidation and both reduce silver nitrate in ammoniacal solution.

It is evident that differences in chemical behavior cannot be attributed merely to differences in the acidic strengths of the boronic acids, and that other factors are more significant. It is suggested that the reduction of ammoniacal silver oxide by aliphatic boronic acids involves the formation of an unstable silver alkyl.

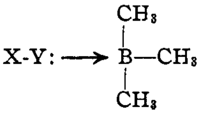
ITHACA, NEW YORK RECEIVED AUGUST 12, 1937

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

Organoboron Compounds. III. Reactions of Tri-*n*-butylborine[1]

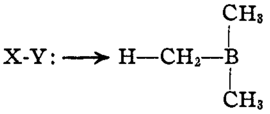
BY JOHN R. JOHNSON, H. R. SNYDER AND M. G. VAN CAMPEN, JR.[2]

The chemical behavior of the alkylborines is of particular interest in considerations of the intimate mechanism of reactions from the standpoint of modern electronic theories. Owing to the absence of unshared electron pairs or multiple bonds within the molecule, a simple alkylborine such as $(CH_3)_3B$ affords an unambiguous example of a system in which the typical reactions can occur *only* through the intervention of electrons from the donor center of a reagent. Reactions of the alkylborines may be initiated by a coördination process in which the open sextet of the 3-covalent boron atom acts as the electron-accepting center, or through the formation of a transient "hydrogen bridge" involving the H–C link of an alkyl group. The two modes of attack are indicated graphically in formulas I and II, where Y represents the active donor center of a reagent X–Y.



$$X\text{-}Y\colon\longrightarrow \overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{B}}\text{—}CH_3$$

(I)



$$X\text{-}Y\colon\longrightarrow H\text{—}CH_2\text{—}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{B}}$$

(II)

Tri-*n*-butylborine was selected as a suitable borine for the purpose of studying reaction mechanisms. The preparation of this borine and its behavior toward several typical reagents are reported in the present paper. A number of alkylborines have been described in the literature but little information is available concerning their reactions.

Frankland[3] prepared trimethyl- and triethylborine by the interaction of zinc alkyls and ethyl borate and observed that they are spontaneously

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[1] This report was presented in part at the Sixth Organic Chemistry Symposium, Rochester, December, 1935. For the preceding papers in the series see THIS JOURNAL, **60**, 105, 111 (1938).

[2] Du Pont Post-Doctorate Research Assistant in Organic Chemistry, 1935–1936.

[3] Frankland and Duppa, *Ann.*, **115**, 319 (1860); Frankland, *ibid.*, **124**, 129 (1862); *J. Chem. Soc.*, **15**, 363 (1862); see also Stock and Zeidler, *Ber.*, **54**, 531 (1921).

inflammable in air. He reported the formation of addition products with ammonia and with potassium hydroxide. Krause and Nitsche[4] prepared a series of trialkyl- and triarylborines by the action of Grignard reagents upon boron trifluoride etherate, and we have obtained tri-*n*-butylborine in good yields (80%) by their method. Tri-*n*-butylborine may be prepared also by the action of *n*-butylmagnesium bromide (in excess) upon methyl borate[5] but the yields are somewhat lower (*ca.* 50% of the theoretical).

The borines may be expected to give rise to quaternary organoboriate anions of the type $[BR_4]^-$ but such compounds have not been obtained hitherto. During the course of the present investigation Thompson and Stevens[6] have reported unsuccessful attempts to obtain quaternary organoboriates. They treated trimethylborine with ethyllithium, methyl- and ethylsodium, and benzylsodium (in ligroin at 120°) but obtained no evidence of reaction. Negative results were also obtained when triphenylborine was treated with methyl- and ethylsodium, and phenyllithium. However, we observed an evolution of heat (sufficient to cause ebullition of the ether) when tri-*n*-butylborine was added to an ethereal solution of phenylmagnesium bromide, and a separation into two liquid phases. When one mole of tri-*n*-butylborine was used per mole of Grignard reagent, the upper layer was found to contain one-half of the borine which remained unattacked. The lower layer containing the quaternary boriate anion $[C_6H_5\text{-}B(C_4H_9)_3]^-$ undergoes hydrolysis with much less vigor than the Grignard reagent itself,[7] yielding benzene and tri-*n*-butylborine. The complex reacted sluggishly and incompletely with phenyl isocyanate to give benzanilide. This behavior indicates clearly that free phenylmagnesium bromide was not present.

Tri-*n*-butylborine also reacts exothermally with an ethereal solution of diphenylmagnesium; separation into two layers occurs as before, but in this case one mole of the borine combines with one mole of the diarylmagnesium. Evidently in both instances there is produced a solvated complex of the type $[C_6H_5Mg(OEt_2)_n]^+$ $[C_6H_5\text{-}B(C_4H_9)_3]^-$. Tri-*n*-butylborine combines exothermally with phenyllithium in ethereal solution, and less vigorously with *n*-butyllithium and *n*-butylmagnesium bromide. In the last three examples the reaction mixture does not separate into two layers. No evidence of reaction was observed when tri-*n*-butylborine and di-*n*-butylzinc were brought together (in the absence of a solvent). The resulting homogeneous liquid was miscible with dry ether, and the ethereal solution obviously contained free di-*n*-butylzinc since it reacted violently with water.[7] Efforts to isolate the magnesium and lithium derivatives of the quaternary boriates in a crystalline state have been unsuccessful, and it appears that the solvent plays an important role in their formation. The failure of earlier attempts to effect combination of the borines with organosodium and lithium compounds[6] was probably due to the use of a hydrocarbon medium, in which solvation does not occur.

The alkylborines differ sharply from the organic derivatives of the neighboring elements beryllium and aluminum, in being stable toward water. However, Frankland[3] observed that triethylborine on heating with strong aqueous hydrochloric acid evolved ethane in an amount corresponding to the elimination of one alkyl group. Our experiments with tri-*n*-butylborine indicate that the cleavage of the borines by hot concentrated solutions of the halogen acids is arrested definitely with the elimination of only one alkyl group. Tri-*n*-butylborine on refluxing with an excess of 48% aqueous hydrobromic acid yielded one mole each of *n*-butane and di-*n*-butylborinic acid (II).

$$(C_4H_9)_3B + HBr \longrightarrow \underset{(I)}{(C_4H_9)_2BBr} + C_4H_{10}$$

$$(C_4H_9)_2BBr + H_2O \longrightarrow \underset{(II)}{(C_4H_9)_2BOH} + HBr$$

$$2(C_4H_9)_2BOH \longrightarrow \underset{(III)}{(C_4H_9)_2B\text{—}O\text{—}B(C_4H_9)_2} + H_2O$$

The latter undergoes dehydration very easily and was isolated in the form of the oxide (III) in 80% of the theoretical amount. Di-*n*-butylboron oxide is a colorless liquid (b. p. 136° at 12 mm.) which shows the normal molecular weight for the formula $(C_4H_9)_2B\text{—}O\text{—}B(C_4H_9)_2$, by the ebullioscopic method in benzene. The oxide is oxidized rapidly in air and ignites spontaneously when spread in a thin film. It is not visibly affected by cold water or cold aqueous alkalies. On

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(4) Krause and Nitsche, *Ber.*, **54**, 2784 (1921); **55**, 1261 (1922).

(5) Khotinsky and Melamed [*ibid.*, **42**, 3090 (1909)] have reported that only one alkoxyl group of methyl borate can be replaced by an alkyl or aryl group in the reaction with RMgX, but their statement is evidently untrue.

(6) Thompson and Stevens, *J. Chem. Soc.*, 556 (1933).

(7) The alkylborines are not hydrolyzed appreciably by water.

heating with *n*-butyl alcohol, with continuous elimination of water, the anhydride is converted smoothly into the *n*-butyl ester of di-*n*-butylborinic acid, $(C_4H_9)_2B{-}OC_4H_9$.

Since the absence of further cleavage may have been due to the rapid hydrolysis of the intermediate bromide (I), experiments were carried out with anhydrous hydrogen bromide. Reaction occurred readily at 55–60° with the formation of exactly one mole of *n*-butane, and di-*n*-butylboron bromide (I) was isolated in almost quantitative yield. Continued action of hydrogen bromide failed to effect any further cleavage. This reaction is quite clear cut and affords access to compounds of the type $R_2B{-}Br$, which have not hitherto been prepared and will be of value in the synthesis of other new types of organoboron compounds.

Tri-*n*-butylborine is not attacked by iodine or bromine in carbon tetrachloride solution (at room temperature), but reacts readily with dry bromine in the absence of a solvent. The reaction is much more complex than that observed with hydrogen bromide. Dealkylation takes place with the formation of *n*-butyl bromide, di-*n*-butylboron bromide and *n*-butylboron dibromide. Substitution in the alkyl groups occurs concurrently, with the formation of hydrogen

$$(C_4H_9)_3B + Br_2 \longrightarrow C_4H_9Br + (C_4H_9)_2BBr$$
$$(C_4H_9)_2BBr + Br_2 \longrightarrow C_4H_9Br + C_4H_9BBr_2$$

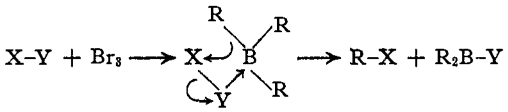
bromide, and the latter reacts in part with the borine to produce *n*-butane and di-*n*-butylboron bromide. A significant feature of this reaction is that bromine is capable of effecting cleavage of two alkyl groups from the borine. The dibromide $C_4H_9BBr_2$ must be formed by the action of bromine on the monobromide $(C_4H_9)_2$-BBr, since the latter has been shown to be inert toward hydrogen bromide.

The reaction of tri-*n*-butylborine with a derivative of hypochlorous acid was also investigated. Pure *t*-butyl hypochlorite (three molar equivalents) was added slowly to the borine at −80° in the absence of a solvent. In spite of the low temperature a vigorous and complex reaction took place. The formation of *n*-butyl chloride (0.33 mole per mole of the borine) indicates a dealkylation of the type

$$(C_4H_9)_3B + ROCl \longrightarrow (C_4H_9)_2BOR + n\text{-}C_4H_9Cl$$

Evidence was also obtained for a substitution reaction involving attack of hydrogen in the alkyl groups, as observed with bromine. In this case the ultimate products appeared to contain butenyl groups (C_4H_7) formed by elimination of hydrogen chloride from the chlorosubstitution product. A halogen-free, unsaturated substance corresponding to the formula $(C_4H_7)_2BOC_4H_9$ was isolated in small amounts.

The dealkylation of tri-*n*-butylborine by a reagent is considered to occur by way of a coördination process in which the electron sextet of the boron atom is temporarily completed by an unshared electron-pair of the reagent molecule (X–Y). The surge of electron density in the direction B ⟶ R increases the mobility of the potential alkyl anion, and an irreversible α,γ-shift within the complex completes the reaction.



In the reaction with hydrogen bromide the bromine atom necessarily acts as electron-donor; with *t*-butyl hypochlorite the oxygen evidently acts as donor, rather than chlorine, since *n*-butyl chloride is formed by the α,γ-transposition. This mode of attack involves separation of "positive" chlorine at the moment of reaction.

Failure of hydrogen bromide to effect further cleavage of alkyl groups to form $RBBr_2$, and eventually BBr_3, may be attributed to a diminished acceptor activity of boron in the monobromide. Owing to the presence of unshared electron pairs on the adjacent bromine atom the acceptor activity of the boron atom can be diminished by an internal effect (resonance)

$$R_2B{-}Br \rightleftarrows R_2\overset{-}{B}{=}\overset{+}{Br}$$

which lowers the intrinsic affinity of boron for an external donor molecule. Coördination between R_2BBr and hydrogen bromide does not produce sufficient mobility of the potential alkyl anion to bring about the irreversible α,γ-transposition. On the other hand, R_2BBr does undergo effective coördination with bromine or with water, leading to $RBBr_2$ and R_2BOH by α,γ-shift in the intermediate complex.

The intimate mechanism of the substitution reaction observed with bromine is more obscure. The occurrence of bromination under very mild conditions may be due to an activating effect of the boron atom upon the adjacent methylene groups, or an activation of bromine molecules by the borine.

Experimental

Tri-*n*-butylborine.—This compound was prepared by adding an ethereal solution of pure methyl borate. or of the etherate of boron trifluoride, to an excess (about 3.2 moles) of *n*-butylmagnesium bromide. Since the preparation of methanol-free methyl borate is a tedious process and the yields of borine are less satisfactory, the boron trifluoride method is preferable. The etherate, $(C_2H_5)_2O—BF_3$, was prepared by passing gaseous boron trifluoride into anhydrous ether, with external cooling, and fractionating the product at atmospheric pressure (b. p. 124–125° at 745 mm.). Boron trifluoride was generated in glass apparatus by the action of concd. sulfuric acid upon a mixture of powdered boric anhydride and either potassium fluoborate[4] or calcium fluoride.[8] Tin foil was used to protect the stoppers.

In a 2-liter three-necked flask equipped with a mercury-sealed stirrer, reflux condenser. dropping funnel and tube for the admission of nitrogen, was placed an ethereal solution containing one mole of *n*-butylmagnesium bromide. The top of the dropping funnel and the reflux condenser were connected to two arms of a Y-tube, the other end of which dipped below the surface of mercury in a test-tube. The apparatus was swept out with a stream of purified nitrogen and a slow stream of nitrogen passed through the apparatus for the duration of the reaction. A solution of 44.7 g. (0.31 mole) of boron trifluoride etherate in 100 cc. of dry ether was added, with stirring, at a rate sufficient to cause gentle refluxing. The addition required about two hours, and the mixture was refluxed gently, with stirring, for an additional two hours. The mixture was then cooled and a solution of 100 cc. of concd. hydrochloric acid in 300 cc. of water added carefully, with stirring. The ether layer was separated, washed with water, 5% sodium bicarbonate solution, and again with water. After drying over magnesium sulfate, the ether was distilled and the residue distilled under reduced pressure. The yield of tri-*n*-butylborine, b. p. 90–91° (9 mm.) or 108–110° (20 mm.), was 45–47 g. (80% yield). All of the manipulations and the distillations were carried out in an atmosphere of nitrogen.

In a similar preparation, using 57.3 g. (0.55 mole) of pure methyl borate and 1.7 moles of *n*-butylmagnesium bromide, the yield of tri-*n*-butylborine was 50 g. (50% of the theoretical). The borine was analyzed for boron by the hydrogen peroxide method.[9]

Anal. Calcd. for $C_{12}H_{27}B$: B, 5.94. Found: B, 5.91, 5.92.

Tri-*n*-butylborine is a colorless, mobile liquid that undergoes oxidation rapidly in the air. When a small quantity of the liquid was placed in a beaker the temperature rose quickly to 90°. When poured onto cotton cloth the liquid ignites spontaneously.

Attempts to prepare a solid addition product of the borine were unsuccessful. No precipitate was formed, and no heat was generated, when a solution of tri-*n*-butylborine in ethanol or benzene was mixed with solutions of the following substances: aniline, methylaniline, *p*-nitroaniline. *p*-anisidine, dimethylamine, triethylamine, *p*-toluenesulfinic acid, thio-*p*-cresol. picric acid. A deep red color appeared on treatment with picric acid, and this color was intensified by heating.

Quaternary Organoboriates.—In a 250-cc. graduated, cylindrical separatory funnel was placed 100 cc. of an ethereal solution containing 0.103 mole of *n*-butylmagnesium bromide (by titration). The neck of the funnel was fitted with a cork bearing a 25-cc. dropping funnel and two 2-mm. glass tubes which served as inlet and outlet for nitrogen. From the dropping funnel 18.8 g. (0.103 mole) of tri-*n*-butylborine was added slowly with shaking. Sufficient heat was evolved to cause the reaction mixture to boil gently. At the completion of the addition the mixture had separated into two layers; the volume of the lower, more viscous layer was 62.5 cc. An additional quantity of 50 cc. of anhydrous ether was added and the mixture was shaken violently. The volume of the lower layer remained unchanged.

There was no evidence of reaction when a small portion of the upper layer was treated with water. The remainder of the upper layer was transferred to a distilling flask and the ether was removed on a steam-bath. The residual liquid was fractionated under reduced pressure (in nitrogen) and gave 8.5 g. of uncombined tri-*n*-butylborine (b. p. 101–106° at 16 mm.). This is 45% of the original material and indicates that the lower layer contained the borine and Grignard reagent in the ratio $(C_4H_9)_3B:2C_6H_5MgBr$.

A small portion of the lower layer containing the quaternary boriate was treated with water. Very little heat was generated but a white, acid-soluble precipitate (magnesium hydroxide) was formed. A 5-cc. portion of the lower layer was treated with phenyl isocyanate; there was no evidence of reaction and no anilide was isolated after hydrolysis. In a similar experiment 5 cc. of the lower layer was treated with phenyl isocyanate and refluxed for thirty minutes. After hydrolysis a small amount of benzanilide, m. p. 158–160°, was isolated. The diminished reactivity of the lower layer toward water and phenyl isocyanate shows clearly that free phenylmagnesium bromide is not present. On standing overnight the lower layer deposited a considerable amount of crystalline material, but this appeared to be mainly an etherate of magnesium bromide contaminated with the organoboriate.

To avoid the influence of magnesium bromide an experiment was carried out with an ethereal solution of diphenylmagnesium, prepared according to the directions of Noller.[10] To 71 cc. of a 0.33 molar solution of diphenylmagnesium (0.023 mole) was added 4.3 g. (0.023 mole) of tri-*n*-butylborine. Very little heat was evolved but the mixture separated into two layers. The upper layer contained only a trace of diphenylmagnesium (less than 0.5% of the original amount), and the lower layer contained the reacting components in the proportion $(C_4H_9)_3B + (C_6H_5)_2Mg$. Consequently, the compound formed in both experiments appears to be a solvated quaternary organoboriate of the formula $[C_6H_5Mg]^+[C_6H_5\text{-}B(C_4H_9)_3]^-$.

A part of the material from the diphenylmagnesium experiment on treatment with water hydrolyzed slowly to give benzene and tri-*n*-butylborine. Another portion was sealed in a glass tube (in an atmosphere of nitrogen) and attempts were made to induce crystallization, but these were unsuccessful.

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(8) Hennion. Hinton and Nieuwland. THIS JOURNAL, **55**, 2858 (1933).

(9) Snyder. Kuck and Johnson, *ibid.*, **60**, 105 (1938).

(10) Noller, *ibid.*, **53**, 635 (1931).

Tri-*n*-butylborine combined with *n*-butylmagnesium bromide with slight evolution of heat but the reaction mixture did not separate into two layers. The resulting homogeneous solution reacted less vigorously with water than *n*-butylmagnesium bromide, but more vigorously than the solution obtained from tri-*n*-butylborine and phenylmagnesium bromide.

Ethereal solutions of *n*-butyllithium and of phenyllithium were prepared according to the method of Gilman[11] and treated with equivalent quantities of tri-*n*-butylborine. Exothermic combination occurred in both cases, but was more vigorous with the aryl compound. All efforts to obtain a crystalline lithium organoboriate were unsuccessful.

There was no evidence of reaction when tri-*n*-butylborine and di-*n*-butylzinc were brought together. The two liquids formed a homogeneous solution which was perfectly miscible with dry ether and reacted violently with water.

Tri-*n*-butylborine and Aqueous Hydrobromic Acid: Di-*n*-butylboron Oxide.—To 75 cc. of 48% aqueous hydrobromic acid, 15.5 g. (0.085 mole) of tri-*n*-butylborine was added and the mixture was refluxed gently. An inflammable gas (*n*-butane) was evolved rapidly at first, and after about one hour the evolution of gas became very slow. The mixture was cooled and transferred to a separatory funnel, using precautions against exposure to air. The organic layer was separated, dissolved in 20 cc. of benzene and washed with 5% sodium carbonate solution, followed by pure water. The solution was dried over anhydrous magnesium sulfate and the solvent was removed. The residue was fractionated under reduced pressure, under nitrogen, and gave 11 g. (80% yield) of di-*n*-butylboron oxide, b. p. 127–130° (13 mm.).

Samples for analysis were prepared by dissolving the crude reaction product in ether, washing with 5% sodium hydroxide and pure water, and continuing the purification in the usual way. Specimens were taken from the fraction boiling at 136° (12 mm.). Boron was determined by the hydrogen peroxide method, and the molecular weight by the ebullioscopic method in benzene.

Anal. Calcd. for $[(C_4H_9)_2B]_2O$: B, 8.14; mol. wt., 266. Found: B, 8.16, 8.19; mol. wt., 260, 247.

Di-*n*-butylboron oxide is a colorless liquid which undergoes oxidation rapidly in the air but does not ignite spontaneously unless spread out in a thin layer on cloth. It does not appear to react with cold water or with cold 20% sodium hydroxide solution.

The *n*-butyl ester of di-*n*-butylborinic acid, $(C_4H_9)_2B-OC_4H_9$, was prepared by heating the oxide with an excess of *n*-butyl alcohol. In a 100-cc. flask fitted with a fractionating column was placed 18.5 g. of the oxide and 18 g. of *n*-butyl alcohol. The mixture was heated gently and the azeotrope of *n*-butyl alcohol and water was distilled off (b. p. 91–92°). After one-half hour the reaction was complete and the temperature of the distilling vapor rose sharply to 115°. The reaction mixture was fractionated under reduced pressure and gave 26 g. (90% yield) of the *n*-butyl ester, b. p. 110–111° (19 mm.). The ester is a colorless liquid which is not hydrolyzed by cold water or cold aqueous alkali.

An attempt was made to prepare phenyl-di-*n*-butylborine by treating the *n*-butyl ester of di-*n*-butylborinic acid with phenylmagnesium bromide. An ethereal solution containing 1 mole of phenylmagnesium bromide was added, with stirring, to a solution of 18.5 g. (0.09 mole) of the butyl ester. Heat was evolved and the reaction mixture separated into two layers. After the addition of the Grignard reagent, which required about one hour, the mixture was stirred and refluxed for two hours longer. The product was treated with dilute hydrochloric acid and the ethereal solution was fractionated under reduced pressure. About two-thirds of the original ester was recovered unchanged, and 2–3 g. of crude benzeneboronic acid was obtained. After crystallization from ether the acid melted at 214–216° (corr.) and gave a precipitate with aqueous mercuric chloride solution.

Tri-*n*-butylborine and Anhydrous Hydrogen Bromide: Di-*n*-butylboron Bromide.—Anhydrous hydrogen bromide from the direct combination of bromine and hydrogen was condensed in a trap cooled in carbon dioxide and acetone. This trap was connected to a tube sealed into the reaction flask and arranged so that the hydrogen bromide would bubble through the liquid. The flask was fitted with a short reflux condenser, the top of which led to a tube of anhydrous calcium chloride. This in turn was equipped with a two-way stopcock so that gases passing through might be diverted into the atmosphere or collected in an inverted graduated cylinder over 20% sodium hydroxide. The graduated cylinder was also provided with a leveling bulb to equalize pressure inside and outside the cylinder. The apparatus was entirely of glass, and all connections were made by ground glass joints.

The apparatus was carefully swept out with 99.5% pure carbon dioxide and 15.7 g. (0.086 mole) of tri-*n*-butylborine placed in the reaction flask. The hydrogen bromide was then allowed to vaporize into the tri-*n*-butylborine and the evolved gases collected in the graduated cylinder. The reaction flask was heated in a water-bath at 55–60° during this period of addition, which took one and one-quarter hours. The apparatus was again swept out with carbon dioxide. The volume of butane evolved was 1020 cc. at 29° and 716 mm. (corrected for vapor pressure of 20% sodium hydroxide) which corresponds to 0.040 mole of butane.

Fractionation of the reaction mixture under reduced pressure gave 7.9 g. (0.0386 mole) of di-*n*-butylboron bromide boiling sharply at 44° at 4 mm., and 8.5 g. (0.0467 mole) of tri-*n*-butylborine, b. p. 65° at 4 mm., was recovered. Briefly summarized, 0.0393 mole of tri-*n*-butylborine gave 0.0386 mole of di-*n*-butylboron bromide and approximately 0.04 mole of *n*-butane.

Di-*n*-butylboron bromide is a colorless liquid which is hydrolyzed readily by cold water. Bromine analyses were carried out by breaking sealed ampoules under water and titrating with standard silver nitrate.

Anal. Calcd. for $C_8H_{18}BBr$: Br, 39.0. Found: Br, 38.39, 38.45.

The bromide did not react at 20° with molecular silver, magnesium amalgam, or 3% sodium amalgam. On heating with 35% sodium amalgam at 40–50° for four hours, a small amount of tri-*n*-butylborine and a black amorphous

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(11) Gilman, Zoellner and Selby, THIS JOURNAL, 55, 1252 (1933).

precipitate (boron)[12] were formed but most of the bromide was recovered unchanged. From 4 g. of the bromide there was obtained 0.5 g. of tri-*n*-butylborine, b. p. 65° (5 mm.), which was identified by analysis.

Tri-*n*-butylborine and Bromine.—A 50-cc. flask was fitted by means of ground glass connections with a dropping funnel and short reflux condenser. The evolved gases were passed through a tube filled with copper tinsel (to remove bromine vapor) and into a trap cooled to −50°. The outlet of the trap was connected to a wash bottle containing a known amount of standard alkali for the absorption of hydrogen bromide.

The apparatus was swept out with pure nitrogen and 14.0 g. (0.077 mole) of tri-*n*-butylborine added through the dropping funnel. The reaction flask was cooled in ice water and 12.3 g. (0.077 mole) of bromine added. The bromine was dried previously by washing three times with an equal volume of concentrated sulfuric acid and a subsequent distillation in all glass apparatus.

Nitrogen was bubbled through the reaction mixture to effect the mixing of the two components. The ice-bath was removed and replaced as necessary to allow the reaction mixture to remain warm without generating enough heat to cause the bromine to boil. After fifteen minutes the reaction was allowed to continue at room temperature, and within an hour the reaction was complete (as evidenced by dissipation of the bromine color). Very little bromine escaped to be absorbed by the copper tinsel. However, some hydrogen bromide was not absorbed in the alkali and escaped. Moreover, it seemed impossible to remove it entirely by bubbling nitrogen gas through the reaction mixture.

The alkali in the wash bottle was titrated to estimate the amount of hydrogen bromide formed. There was originally present 0.1131 mole of alkali; final titration showed a remainder of 0.0788 mole. Hence 0.0343 mole or 2.77 g. of hydrogen bromide was absorbed by the alkali.

The condenser trap for the effluent gases contained a clear, colorless liquid which boiled from 0–2° and burned with a luminous flame. Much of this material was lost but about 1 g. (0.017 mole) was isolated. The substance did not decolorize bromine water and was undoubtedly *n*-butane.

The reaction mixture was subjected to fractional distillation under nitrogen. The first fraction was *n*-butyl bromide (b. p. 99–100°) and weighed 3.8 g. (0.0277 mole). It was identified by formation of the Grignard reagent and conversion to *n*-butylmercuric bromide, m. p. 129°, and *n*-valeranilide, m. p. 62°.

The distillation was continued under reduced pressure. The second fraction, collected at about 65° at 23 mm., weighed 1.5 g. and contained some *n*-butyl bromide. The material was purified by redistillation and identified as *n*-butylboron dibromide by analysis.

Anal. Calcd. for $C_4H_9BBr_2$: Br. 70.2. Found: Br, 68.9. 69.1.

The third fraction, b. p. 88–90° (23 mm.), weighed 7.5 g. and was identified as di-*n*-butylboron bromide by analysis. The fourth fraction, b. p. 66–67° (5 mm.), weighed 2 g. and was unreacted tri-*n*-butylborine. The last fraction, b. p. 104–120°, did not contain halogen; it was not identified. The residue in the distilling flask weighed 2.0 g. and upon exposure to moisture or air gave a white waxy solid. This material was not identified.

When correction was applied for the recovered borine, it was found that one mole of tri-*n*-butylborine had reacted with 1.15 moles of bromine. The approximate quantities of the products actually identified were: 0.5 mole of HBr. 0.3 mole of *n*-butane, 0.4 mole of *n*-C_4H_9Br, 0.1 mole of *n*-$C_4H_9BBr_2$ and 0.56 mole of $(n\text{-}C_4H_9)_2B$—Br.

Tri-*n*-butylborine and *t*-Butyl Hypochlorite.—The hypochlorite was prepared from *t*-butyl alcohol and sodium hypochlorite by the method of Chattaway.[13] It was carefully fractionated to remove acetone and other impurities and used immediately. In preliminary experiments an effort was made to follow the reaction quantitatively by using standard solutions of the hypochlorite in either pure chloroform or ligroin, but this procedure was unsatisfactory. Consequently the reaction was effected at −80° in the absence of a solvent.

In a small two-necked flask, fitted with a 35-cm. modified Podbielniak fractionating column and a dropping funnel and filled with nitrogen, was placed 16 g. (0.09 mole) of tri-*n*-butylborine. The reaction flask was cooled in a bath of acetone and solid carbon dioxide and 28.5 g. (0.27 mole) of *t*-butyl hypochlorite added very slowly from the dropping funnel. The reaction was quite vigorous. The reaction mixture was allowed to warm up slowly to room temperature and carefully fractionated:

(1) The first fraction was *t*-butyl chloride, b. p. 50–54°. The material weighed 3 g. (0.03 mole) and was identified by conversion into trimethylacetanilide, m. p. 123–125° (uncorr.).

(2) This fraction, b. p. 78–81°, was a mixture of *n*-butyl chloride and *t*-butyl alcohol, which were separated by treatment with water. The *t*-butyl alcohol was distilled from the water solution, dried and identified as the α-naphthylurethan, m. p. 133–134°. The yield was about 8 g. of crude alcohol (0.092 mole). The *n*-butyl chloride was dried over barium oxide and identified by conversion to *n*-valeranilide, m. p. 59–61° (uncorr.). The yield was about 3 g. (0.03 mole).

(3) This fraction was identified as 1,1-dichloroacetone; the yield was 3 g. (0.023 mole). It boiled from 110–120°, contained halogen, and was heavier than water. It gave no test for an aldehyde group with Schiff's reagent nor for unsaturation with bromine in carbon tetrachloride. It reacted with *m*-dinitrobenzene in alkaline solution to give a red color which changed to brown (test for the —CH_2—CO—group). Upon warming with aqueous hydroxylamine a product was obtained which melted from 149–152° (uncorr.), after two recrystallizations from alcohol. The melting point of methylglyoxime is 153°.

(4) This fraction amounted to about 2.5 g., b. p. 55–60° at 5 mm. It was redistilled and the boiling points observed were 35° at 5 mm., and 156° at 745 mm. It contained halogen, and was heavier than water. It was not affected perceptibly by air, nor did it appear to react with sodium. After shaking with water at 80° it failed to give a test for

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[12] Since the completion of this work Wiberg and Ruschmann [*Ber.*, **70**, 1583 (1937)] have prepared dimethylboron chloride and observed that it reacts with sodium in a similar way, to give trimethylborine and boron.

[13] Chattaway, *J. Chem. Soc.*, **123**, 3000 (1923).

aldehyde with either ammoniacal silver nitrate or Schiff's reagent. However, the aqueous hydrolysate contained *n*-butyl alcohol. This was extracted with ligroin and identified as the dinitrobenzoate, m. p. 63–64°, and the α-naphthylurethan, m. p. 68–70°.

(5) This fraction was collected at 87–97° (5 mm.), and upon redistillation gave 3 g. of material boiling at 70–71° (4 mm.). It contained boron but not halogen. Upon exposure for one to two hours to air, and subsequent hydrolysis, a positive test for aldehyde was obtained with ammoniacal silver nitrate or Schiff's reagent. This behavior and the boron content suggest that the compound may be a butyl ester of di-*n*-butenylborinic acid.

Anal. Calcd. for $(C_4H_7)_2B—OC_4H_9$: B, 5.58. Found: B, 5.51, 5.54.

(6) Further distillation took place with marked decomposition and no definite boiling point could be assigned. The distillate contained no halogen; it ignited when absorbed on cotton and exposed to air, and reacted with bromine in carbon tetrachloride. It is probably a tributenylborine, formed by loss of hydrogen chloride from a chlorinated tri-*n*-butylborine.

Summary

Tri-*n*-butylborine has been prepared and its behavior toward several reagents has been studied.

Anhydrous hydrogen bromide brings about quantitatively the cleavage of one alkyl group, with the production of *n*-butane and di-*n*-butylboron bromide, $(C_4H_9)_2B—Br$. The latter is a representative of a class of aliphatic boron compounds that had not been prepared hitherto. Aqueous hydrobromic acid effects likewise a quantitative cleavage of one alkyl group, producing *n*-butane and di-*n*-butylborinic acid, $(C_4H_9)_2B—OH$. The latter undergoes dehydration to the corresponding oxide, $(C_4H_9)_2B—O—B(C_4H_9)_2$.

Tri-*n*-butylborine is dealkylated by bromine (anhydrous) to yield principally *n*-butyl bromide and di-*n*-butylboron bromide. Further dealkylation to form *n*-butylboron dibromide occurs to a limited extent. The reaction of bromine also involves substitution in the hydrocarbon residue of the borine.

Dealkylation and chlorination were also observed with *t*-butyl hypochlorite.

The electronic interpretation of these reactions is discussed.

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[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

Organoboron Compounds. IV. Reaction of Tri-*n*-butylborine with Peroxides and with Oxygen. Mechanism of Autoöxidation

BY JOHN R. JOHNSON AND M. G. VAN CAMPEN, JR.[1]

Recent studies of the dealkylation of tri-*n*-butylborine by anhydrous hydrogen bromide and concentrated aqueous hydrobromic acid have shown that these reagents bring about a quantitative cleavage of one alkyl group. With anhydrous bromine some substitution was observed, as well as cleavage of one or two alkyl groups.[2] The present report deals with the behavior of tri-*n*-butylborine toward peroxides and molecular oxygen.

Aqueous hydrogen peroxide, in the presence of dilute alkalies, effects a complete dealkylation of tri-*n*-butylborine with the formation of boric acid and *n*-butyl alcohol. The reaction is rapid and quantitative, and can be used as the basis of a convenient method for the determination of boron in organoboron compounds. Benzoyl peroxide and perbenzoic acid react readily with tri-*n*-butylborine at 0° in chloroform solutions. The reaction of perbenzoic acid is practically quantitative and results in the cleavage of all three of the alkyl groups. Three moles of perbenzoic acid were reduced per mole of the borine, and after treatment with cold dilute alkali *n*-butyl alcohol was isolated; no butyl benzoate was formed in the reaction. The observed results may be expressed by the following equations

$$R_3B + 3C_6H_5CO_3H \longrightarrow B(OR)_3 + 3C_6H_5CO_2H$$
$$B(OR)_3 + 3H_2O \longrightarrow 3ROH + H_3BO_3$$

The trialkylborines react vigorously with atmospheric oxygen, and the lower members of the series are spontaneously inflammable in the air. By very slow autoöxidation of triethylborine Frankland[3] obtained the diethyl ester of ethaneboronic acid, which gave the boronic acid and ethyl alcohol on treatment with water. Krause[4]

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[1] Du Pont Post-Doctorate Research Assistant in Organic Chemistry, 1935–36.

[2] Johnson, Snyder and Van Campen, THIS JOURNAL, **60**, 115 (1938).

[3] Frankland, *J. Chem. Soc.*, **15**, 363 (1862).

[4] Krause and collaborators, *Ber.*, **61**, 278 (1928); **63**, 934 (1930).