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, $(C_4H_9)_2$-B—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.

[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

$$R_3B + 3C_6H_5CO_3H \longrightarrow B(OR)_3 + 3C_6H_5CO_2H$$
$$B(OR)_3 + 3H_2O \longrightarrow 3ROH + H_3BO_3$$
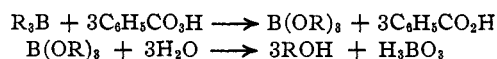
The trialkylborines react vigorously with atmospheric oxygen, and the lower members of the series are spontaneously inflammable in the air. By very slow autoöxidation of triethylborine Frankland[3] obtained the diethyl ester of ethaneboronic acid, which gave the boronic acid and ethyl alcohol on treatment with water. Krause[4]

(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).

examined a number of trialkylborines and concluded that the normal autoöxidation (controlled by slow admission of air) gives rise to esters of the aliphatic boronic acids or to the alkylboron oxides. He did not isolate and identify these products but showed that the alkaneboronic acids were produced upon hydrolysis. In the present study, two series of autoöxidation experiments were carried out with tri-n-butylborine, one under anhydrous conditions and the other in the presence of water, using air as the source of oxygen.

Quantitative experiments showed that pure anhydrous tri-n-butylborine combines with one mole of oxygen to give the n-butyl ester of 1-butaneboronic acid. The latter was isolated in a pure state and on hydrolysis gave 1-butaneboronic

$$R_3B + O_2 \text{ (dry)} \longrightarrow RB(OR)_2$$
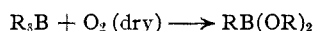
acid and n-butyl alcohol. The oxidation was clear-cut and there was no evidence of any other product.[5]
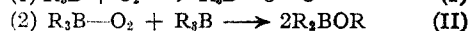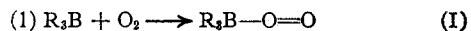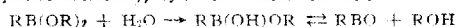
In the presence of water the oxidation process consumes only one-half mole of oxygen and is arrested neatly at the half-way stage. The n-butyl ester of di-n-butylborinic acid was isolated in 92% of the theoretical amount. Only a small amount of the ester was hydrolyzed during the oxidation, and that portion was isolated in the form of di-n-butylboron oxide (R_2BOBR_2). Autoöxidation in the presence of water is represented therefore by the equation

$$2R_3B + O_2 \text{ (moist)} \longrightarrow 2R_2BOR$$
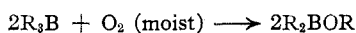
This observation suggests that anhydrous autoöxidation is a stepwise process in which the dialkylborinic ester is an intermediate product, and that water inhibits further oxidation of the latter.

Frankland's observation that the ammonate of trimethylborine is stable toward atmospheric oxygen, and other indirect evidence, supports the hypothesis that autoöxidation proceeds by way of an intermediate complex in which the oxygen molecule acts as electron-donor. The primary adduct or unstable "borine—peroxide" (I) then reacts with a second molecule of the borine to produce two molecules of the dialkylborinic ester (II) in a manner analogous to the interaction of peracetic acid and acetaldehyde to give two molecules of acetic acid.

(5) The formation of alkylboron oxides, reported by Krause,[4] may be attributed to hydrolysis of the ester by a limited amount of water (atmospheric moisture), *after* the initial oxidation:

$$RB(OR)_2 + H_2O \longrightarrow RB(OH)OR \rightleftarrows RBO + ROH$$

$$\text{(1) } R_3B + O_2 \longrightarrow R_3B\text{—}O\text{=}O \qquad \text{(I)}$$
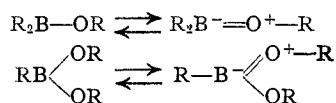$$\text{(2) } R_3B\text{—}O_2 + R_3B \longrightarrow 2R_2BOR \qquad \text{(II)}$$

In a similar way (under anhydrous conditions) the dialkylborinic ester is oxidized to the boronic ester, but the oxidation ends at this point. However, it has been shown previously that *free* aliphatic boronic acids undergo oxidation in dry air but are unaffected when moisture is present.[6]

A survey of the behavior of various alkyl boron compounds toward hydrogen bromide, bromine, perbenzoic acid, hydrogen peroxide and molecular oxygen indicates a definite gradation of reactivities. Cleavage of the boron-alkyl linkage occurs less readily as the alkyl groups of the borine are replaced successively by halogen, hydroxyl or alkoxyl groups.

$$R_3B > R_2BX > RBX_2$$
$$R_3B > R_2BOH > RB(OH)_2$$
$$R_3B > R_2BOR > RB(OR)_2$$
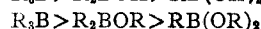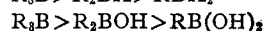
Perbenzoic acid and hydrogen peroxide bring about complete dealkylation of BR_3; bromine and dry oxygen are capable of cleaving two alkyl groups, hydrogen bromide and moist oxygen only one.

The observed gradations support the view that the reactivity of the alkyl organoboron compounds toward a given donor molecule is diminished by the attachment of atoms or groups which contain unshared electron pairs (–Br, –OH, –OR) and are capable of giving rise to resonance effects

$$R_2B\text{—}OR \rightleftarrows R_2B^-\text{=}O^+\text{—}R$$
$$RB\begin{array}{c}\diagup OR \\ \diagdown OR\end{array} \rightleftarrows R\text{—}B\begin{array}{c}\diagup O^+\text{—}R \\ \diagdown OR\end{array}$$

The introduction of groups such as Br, OH and OR, tends to bring about an inductive effect of electron withdrawal from the boron atom ($B{\rightarrow}X$ relative to B–R), which would increase its electron deficit and its acceptor activity, but the dynamic effect is in the opposite direction ($B{\overset{\frown}{\leftarrow}}X$) and compensates the deficient boron atom.

A salient feature of the inhibiting action of water upon autoöxidation of the various organoboron compounds is that it does not inhibit autoöxidation of the trialkylborine but is effective for compounds containing an alkoxyl or hydroxyl group attached to boron. It seems clear that the inhibition mechanism involves the presence of the linkage –B–O– and it is possible that the ability of these compounds to form more stable hydrates than the borines is responsible for arresting the

(6) Snyder, Kuck and Johnson, THIS JOURNAL, **60**, 105 (1938).

autoöxidation. Further experiments on the auto-oxidation mechanism and the effects of foreign substances are in progress.

Experimental

Oxidation of Tri-*n*-butylborine by Perbenzoic Acid.—Small sealed ampoules of pure tri-*n*-butylborine[2] (0.25–0.30 g.) were broken under 15–20 cc. of pure chloroform in a nitrogen-filled flask, and an excess of standardized solution of perbenzoic acid was pipetted into each flask and mixed well by shaking. The perbenzoic acid was used in chloroform solution and standardized iodimetrically immediately before use.[7] After standing for three hours at 20°, the excess perbenzoic acid was determined iodimetrically. In three typical experiments the following quantities of perbenzoic acid were consumed: 2.933, 2.855, 2.910 (moles $C_6H_5CO_3H$ per mole of BR_3). These results indicate that the oxidation of the borine by perbenzoic acid is essentially quantitative and requires three equivalents of the peroxide.

In another experiment the nature of the oxidation product was investigated. A chloroform solution (210 cc.) containing 0.113 mole of perbenzoic acid, in a nitrogen-filled flask, was cooled thoroughly in an ice–salt bath and 6.5 g. (0.035 mole) of tri-*n*-butylborine was added. During the addition the temperature was kept below 5°; the solution was then removed from the cooling bath and allowed to stand at 20° for four hours. The chloroform solution was then washed with cold 5% sodium hydroxide solution, followed by pure water, and dried over anhydrous calcium chloride (through an unfortunate error). After distilling off the chloroform through a good column, there was obtained 3.6 g. (0.05 mole) of *n*-butyl alcohol, b. p. 117°. There was no evidence of any butyl benzoate. Undoubtedly an appreciable amount of *n*-butyl alcohol was lost by the use of calcium chloride as drying agent.

Quantitative experiments were carried out also with tri-*n*-butylborine and standardized solutions of benzoyl peroxide in chloroform, but the results were very irregular. Although efforts were made to carry out the reactions under uniform conditions, the quantity of benzoyl peroxide consumed varied from 1.8 to 4.2 moles (per mole BR_3) in different experiments. Further study of this reaction will be carried out in connection with the investigation of the reducing action of tri-*n*-butylborine on other substances.

In the course of this investigation Meerwein and his collaborators[8] have reported the reduction of various carbonyl compounds by triethylborine.

Autoöxidation of Tri-*n*-butylborine.—Quantitative measurements were made to determine the amount of oxygen taken up by tri-*n*-butylborine under anhydrous conditions, and in the presence of water. In other experiments, with larger amounts of material, the oxidation products were isolated in a pure state and identified.

Oxidation under Anhydrous Conditions.—(a) The top of a 50 cc. buret was fitted to a 500-cc. filtering flask, the side-arm of which was connected to a tube for breaking thin-walled sample bulbs as described by Stock.[9] A thin-

(7) *Org. Syntheses*, **13**, 89 (1933).
(8) Meerwein, *J. prakt. Chem.*, [2] **147**, 232 (1936).
(9) Stock and Zeidler, *Ber.*, **54**, 553 (1921).

walled ampoule containing 0.1217 g. (0.67 millimole) of pure tri-*n*-butylborine was placed in this tube, the apparatus swept out with dry air, and the bottom of the buret attached to a leveling bulb filled with mercury. The stopper of the sample-breaking tube was fitted tightly and the level of the mercury noted in the buret, as well as the prevailing barometric pressure and temperature. The sample tube was then crushed and the reaction allowed to proceed until no further diminution of volume occurred. The final buret reading was made at the same pressure and temperature as the original reading, thus obviating correction for the volume of the system. The absorption of oxygen amounted to 16.4 cc. at 739 mm. and 26°, which is equivalent to 0.65 millimole. This result shows that one mole of the borine reacted with 0.97 mole of oxygen, and leads to the belief that the only reaction probably proceeds to form the dibutyl ester of butylboric acid. This view was substantiated by the following experiment.

(b) A sample of tri-*n*-butylborine was allowed to stand for six months in a test-tube closed with a porous cork, so that air diffused slowly into the tube. At the end of this period the material was distilled through a 35-cm. modified Podbielniak column. Only one fraction was obtained, which boiled sharply at 110–111° at 24 mm. The product was a clear, colorless liquid which was not visibly affected by air, even when absorbed on cotton. It was hydrolyzed very slowly by warm water, but fairly rapidly by warm 6 *N* hydrochloric acid. By chilling the hydrolysate in ice water and filtering, a crystalline solid was isolated which was identified as 1-butaneboronic acid, m. p. 90–92°. By ether extraction of the filtrate and evaporation of the ether a liquid was obtained which yielded a 3,5-dinitrobenzoate, m. p. 63–64.5°. The m. p. was not depressed when mixed with an equal amount of authentic *n*-butyl 3,5-dinitrobenzoate. These data clearly indicate that tri-*n*-butylborine is oxidized by dry air to the di-*n*-butyl ester of 1-butaneboronic acid.

Oxidation by Moist Air.—(a) This experiment was carried out in the same way as the quantitative oxidation with dry air already described, except that water was introduced into the filter flask and reaction tube. Water vapor was allowed to saturate the air before the initial buret reading was made. Under these conditions a sample of the borine weighing 0.1147 g. (0.63 millimole) absorbed 7.41 cc. of oxygen at 737 mm. and 26° (0.293 millimole). These figures indicate that one mole of tri-*n*-butylborine reacted with 0.465 mole (0.93 gram-atom) of oxygen, and the reaction may therefore be expected to yield the *n*-butyl ester of di-*n*-butylborinic acid, $(C_4H_9)_2B-OC_4H_9$.

(b) A sample of 2.0 g. (0.011 mole) of tri-*n*-butylborine was placed in a small two-necked flask fitted with a 35-cm. modified Podbielniak column and a capillary tube for the admission of air. About 0.5 cc. of water was added to the borine and moist air forced through the capillary tube for twelve hours. The volume of air passed through was roughly equivalent to 0.01 mole of oxygen.

The water was then removed by reducing the pressure and keeping the temperature of the reaction mixture below 20–25°. The distillate was condensed in a receiver cooled in ice and salt. It consisted of pure ice, was homogeneous upon melting, and contained no traces of octane or dibutyl ether. When the reaction mixture was distilled only one

fraction was obtained, b. p. 120–121° at 24 mm. The yield was 2 g., or 92% of the theoretical amount based on tri-n-butylborine. The boiling point of a specimen of n-butyl dibutylborinate synthesized from di-n-butylboron oxide and n-butyl alcohol[2] was 110° at 19 mm., which agrees satisfactorily with the boiling point observed in this case. Previous observations showed that this ester does not react appreciably with either water or 10% sodium hydroxide, and this explains the failure of the ester to be hydrolyzed appreciably by the water present during the oxidation.

The small residue from this distillation, when absorbed on cotton and exposed to air, became hot and the cotton was charred. This behavior is characteristic of di-n-butylboron oxide, which would be formed by hydrolysis of the butyl ester of di-n-butylborinic acid and subsequent dehydration. The amount of residue obtained in this case was too small for a determination of its boiling point.

Summary

The behavior of tri-n-butylborine toward hydrogen peroxide, perbenzoic acid and molecular oxygen has been studied.

Hydrogen peroxide and perbenzoic acid oxidize the borine quantitatively with the formation of n-butyl alcohol and boric acid.

In the absence of water tri-n-butylborine combines with one mole of oxygen to form di-n-butyl n-butylboronate, C_4H_9–$B(OC_4H_9)_2$. In the presence of water only half as much oxygen is consumed and the product is n-butyl di-n-butylborinate, $(C_4H_9)_2B$–OC_4H_9.

The mechanism of the oxidation process and of the inhibiting action of water is discussed.
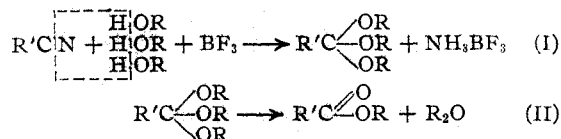

Organic Reactions with Boron Fluoride.[1] XVII

BY JAMES F. MCKENNA[2] AND FRANK J. SOWA

The purpose of this paper is to present several short investigations that were performed in the presence of boron fluoride. The reactions considered are: the formation of phenolphthalein and fluorescein from the action of phthalic anhydride with phenol and resorcinol, the formation of ethers and esters from the reaction of nitriles and alcohols; the formation of anilides from the reaction of esters with aniline and the alkylation of phenols by alcohols.

Fluorescein and phenolphthalein were prepared at a low temperature and in a short period of time by using boron fluoride as a condensing agent.

In previous publications[3,4] boron fluoride has been shown to function very desirably as an agent to remove the elements of ammonia. The boron fluoride appeared as monoamminoboron fluoride. In the present study monoamminoboron fluoride was eliminated in the reaction of nitriles with alcohols

$$R'C\!\!:\!\!N + \overset{\overline{H}|OR}{\underset{H|OR}{H|OR}} + BF_3 \longrightarrow R'C\!\!\underset{OR}{\overset{OR}{\diagdown}}\!\!-OR + NH_3BF_3 \quad (I)$$

$$R'C\!\!\underset{\diagdown OR}{\overset{OR}{\diagup}}\!\!-OR \longrightarrow R'C\!\!\overset{O}{\diagdown}\!\!-OR + R_2O \quad (II)$$

Under the conditions of the reaction the assumed ortho ester (equation I) decomposed to an ester and an ether (equation II). The latter reaction was confirmed by treatment of ethyl orthoformate with boron fluoride to give diethyl ether–boron fluoride and ethyl formate–boron fluoride.

Aniline reacts with esters to give very poor yields of anilides and alcohols. The yields of anilides were only 2 to 10%.

t-Butyl alcohol and i-butyl alcohol reacted with phenol to give the identical product, p-t-butylphenol as the main product. This gives further confirmation of the intermediate olefin formation before alkylation of the phenol.[5]

Experimental Part

Preparation of Fluorescein.—By refluxing a mixture of phthalic anhydride (60 g.), resorcinol (50 g.) and boron fluoride (8 g.) in 100 g. of benzene for three hours, a reddish mass insoluble in benzene was obtained. The benzene was removed and the remaining mass purified in the usual manner.[6] Practically the theoretical yield of fluorescein was obtained. The diacetate derivative[7] melted at 203–205°.

Preparation of Phenolphthalein.—This procedure was somewhat similar to the preparation of fluorescein except that no benzene was used. Phthalic anhydride (0.75 mole), phenol (1.5 moles) and 50 g. of boron fluoride were heated carefully for one hour. A 72% yield of crude phenolphthalein was isolated.

(1) Original manuscript received June 25, 1937. For previous paper see Croxall, Sowa and Nieuwland, J. Org. Chem., 2, 253 (1937).

(2) Garvan Fellow.

(3) Sowa and Nieuwland, THIS JOURNAL, 55, 5052 (1933).

(4) Idem., 59, 1202 (1937).

(5) Sowa, Hennion and Nieuwland, ibid., 57, 709 (1935).

(6) Baeyer, Ann., 183, 3 (1876).

(7) Von Liebig, J. prakt. Chem., 85, 241 (1912).