## Summary

A number of primary aliphatic boronic acids have been prepared and their chemical behavior has been investigated. These acids were found to be inert toward various reagents which effect cleavage of the boron–carbon bond of the aromatic boronic acids.

The anhydrous boronic acids undergo autoxidation in air but the presence of water inhibits the oxidation. Aqueous hydrogen peroxide converts the boronic acid to the corresponding alcohols and boric acid. The primary aliphatic boronic acids reduce silver nitrate in ammoniacal solution with the production of one equivalent of metallic silver and the hydrocarbon R–R.

Dehydration of the boronic acids yields alkylboron oxides, which are cyclic trimers analogous to paraldehyde.

ITHACA, NEW YORK RECEIVED AUGUST 12, 1937

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

# Organoboron Compounds. II. The Reducing Action of Some Organoboronic Acids[1]

BY JOHN R. JOHNSON, M. G. VAN CAMPEN, JR.,[2] AND OLIVER GRUMMITT[2]

In 1882 Michaelis and Becker[3] reported the formation of a silver mirror when benzeneboronic acid ("phenylboric acid") was warmed with silver nitrate in ammoniacal solution and observed that benzene was the principal organic product of the reaction. Other typical aromatic boronic acids have been found to behave similarly and this reaction has proved useful as a general method for eliminating the $-B(OH)_2$ group from substituted benzeneboronic acids.[4]

Although the formation of a silver mirror has sometimes been regarded as a characteristic test for aromatic boronic acids, the principal reaction that occurs with ammoniacal silver oxide must be formulated as a hydrolytic cleavage and not a reduction.

$$C_6H_5\text{–}B(OH)_2 + H\text{–}OH \xrightarrow{[Ag(NH_3)]^+} C_6H_5\text{–}H + H_3BO_3$$

This reaction does not account for the production of any metallic silver; indeed, careful examination of the products from benzene- and *p*-tolueneboronic acids reveals that only a minute quantity of metallic silver is actually produced. It is of interest to note that a similar hydrolytic cleavage of aromatic boronic acids occurs on warming with cadmium or zinc halides.[5]

Earlier investigators reported that typical aliphatic boronic acids reduce silver nitrate in ammoniacal solution, and a study of primary aliphatic boronic acids in This Laboratory[6] showed that the reduction produces one equivalent of metallic silver and the hydrocarbon R–R. The marked difference between the aryl and alkyl derivatives suggested that the study of a series of organoboronic acids might reveal a definite relation between the structure of organic radicals and the reducing action of their organometallic derivatives. This subject is of particular interest in relation to Grignard reagents, where the reducing action occurs as an abnormal reaction.

The behavior of organoboronic acids containing the *n*-butyl, *n*-hexyl, phenyl and *p*-tolyl groups toward ammoniacal silver nitrate has already been studied. The benzyl, *t*-butyl, 2-furyl and 2-thienyl analogs were chosen as a representative selection of organoboronic acids for further investigation. These were obtained by reaction of the appropriate Grignard reagents with an excess of methyl borate at low temperature, and hydrolysis of the resulting organoboronic ester.

α-Tolueneboronic acid ("benzylboric acid") proved to be much more susceptible to atmospheric oxidation than the typical primary aliphatic boronic acids. Even in the presence of water, which inhibits the atmospheric oxidation of 1-butaneboronic acid, the benzyl compound undergoes autoöxidation to boric acid and benzyl alcohol. α-Tolueneboronic acid is not appreciably decomposed by hot water or hot 5% sulfuric acid, but is hydrolyzed rapidly and quantitatively by hot 5% sodium hydroxide solution to give

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[1] This report is part of a paper presented at the Sixth Organic Chemistry Symposium, Rochester, December, 1935. For the first paper of the series see Snyder, Kuck and Johnson, THIS JOURNAL, **60**, 105 (1938).

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[3] Michaelis and Becker, *Ber.*, **15**, 181 (1882).

[4] Seaman and Johnson, THIS JOURNAL, **53**, 711 (1931); Bean and Johnson, *ibid.*, **54**, 4415 (1932).

[5] Ainley and Challenger, *J. Chem. Soc.*, 2171 (1930). Reducing action of aromatic boronic acids was observed with cupric halides and sulfate.

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

toluene and boric acid. With ammoniacal silver oxide an instantaneous precipitation of metallic silver occurs and dibenzyl is formed. This reaction, like that of 1-butaneboronic acid, yields one gram atom of silver and one-half mole of hydrocarbon R–R per mole of the organoboronic acid.

$$2C_6H_5CH_2B(OH)_2 + O_2 + 2H_2O \longrightarrow 2C_6H_5CH_2OH + 2H_3BO_3$$

$$C_6H_5CH_2B(OH)_2 + H_2O(NaOH) \longrightarrow C_6H_5CH_3 + H_3BO_3$$

$$2C_6H_5CH_2B(OH)_2 + 2[Ag(NH_3)]^+ \longrightarrow C_6H_5CH_2CH_2C_6H_5 + 2Ag + H_3BO_3 + 2[NH_4]^+$$

2-Methylpropane-2-boronic acid ("*t*-butylboric acid") is similar to the benzyl compound in its unusual ease of autoöxidation. However, the reaction with ammoniacal silver oxide is different from that observed with any other organoboronic acid. One mole of the acid produced 1.9 gram atoms of silver, and the main organic product was *t*-butyl alcohol. The principal reaction is represented by the equation

$$(CH_3)_3C{-}B(OH)_2 + 2[Ag(NH_3)]^+ + 2H_2O \longrightarrow (CH_3)_3C{-}OH + H_3BO_3 + 2Ag + 2[NH_4]^+$$

The characteristic, camphene-like odor of hexamethylethane was noticed, but evidently only a trace was formed and it could not be isolated. Small amounts of isobutane and isobutylene were identified.

2-Furanboronic acid was found to exist in two forms: one, m. p. 110° (dec.), was obtained by crystallization from water; another, m. p. 122°, from benzene or toluene. Determination of neutralization equivalents showed that both forms correspond to the anhydrous acid, $C_4H_3O{-}B(OH)_2$. Neither form is oxidized appreciably on standing in the air. With aqueous silver nitrate or ammoniacal silver oxide, the acid produces a bright orange precipitate of the silver salt. Upon warming in the presence of water, the salt decomposes with evolution of furan and leaves a perfectly clear solution with no evidence of any metallic silver. In this reaction, and in the ease of cleavage of the boron–carbon linkage by other reagents, 2-furanboronic acid is like the aromatic boronic acids. It reacts readily with aqueous mercuric chloride to give 2-chloromercurifuran, with cupric chloride or bromide to give the cuprous halide and 2-halofuran, and with iodine to give 2-iodofuran.

2-Thiopheneboronic acid proved to be strikingly similar to the furan analog in its chemical behavior. With aqueous silver nitrate a yellow silver salt is produced, and on warming the aqueous suspension thiophene is formed without any metallic silver. The acid also undergoes replacement reactions with mercuric chloride, with cupric halides and with iodine. 2-Furan- and 2-thiopheneboronic acids can be titrated easily in the presence of mannitol with standard alkali.

The behavior of the four organoboronic acids examined confirms the sharp distinction between the aliphatic acids and those having a group of aromatic character (phenyl, *p*-tolyl, 2-furyl or 2-thienyl) attached directly to the boronic acid residue. The alkyl compounds are known to be much weaker acids but the strength of the organoboronic acid seems to bear no direct relation to the stability of the boron–carbon linkage. α-Tolueneboronic acid[7] is a stronger acid than the aliphatic compounds and is about the same strength as the simple aromatic boronic acids, yet it behaves like the primary aliphatic boronic acids toward ammoniacal silver oxide.

Some significance may be attached to the circumstance that the boronic acids which undergo hydrolytic cleavage (aromatic types) give rise to definite silver salts as intermediate products, whereas those which bring about reduction (alkyl types) give no evidence of the formation of such salts. This suggests that the reduction may occur through an unstable organosilver compound which is formed from the alkyl compounds and not from the aromatic types.

$$n\text{-}C_4H_9B(OH)_2 + [Ag(NH_3)]^+ + H_2O \longrightarrow n\text{-}C_4H_9Ag + H_3BO_3 + [NH_4]^+ \quad 2n\text{-}C_4H_9Ag \longrightarrow 2Ag + C_8H_{18}$$

There is at present no definite evidence to support this hypothesis since little information is available concerning the silver alkyls, except that they are known to be extremely unstable. The observation that benzyl- and *n*-butylmagnesium halides react with silver bromide to yield the hydrocarbons R–R and metallic silver[8] affords some evidence that the silver alkyls decompose in the manner suggested, since one may expect the silver alkyls to be formed as intermediates in the reaction of organomagnesium compounds with silver halides.

A suitable interpretation of the anomalous behavior of the *t*-butyl acid must await the results of further work in this field. At present no experimental data are available for boronic acids containing a secondary alkyl group attached to boron; one may expect these to be intermediate between the primary and tertiary compounds.

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(7) Yabroff, Branch and Bettman, THIS JOURNAL, **56**, 1852 (1934).

(8) Gardner and Borgstrom, *ibid.*, **51**, 3377 (1929).

The preparation of several compounds of this type (*s*-butyl, cyclopentyl, and cyclohexyl) and studies of their reducing action are now in progress.

## Experimental

**α-Tolueneboronic Acid ("Benzylboric Acid").**—This acid was prepared by the same general procedure described for 1-butaneboronic acid.[6] The slow addition of 0.5 mole of benzylmagnesium chloride to 55 g. (0.53 mole) of methyl borate, in ethereal solution at −70°, gave 65–70 g. of the crude moist acid (50% yield). Samples were purified as needed by crystallization from water or benzene; m. p. 104°. α-Tolueneboronic acid has been prepared previously by Khotinsky and Melamed (m. p. 161°),[9] by Krause (m. p. 161°),[10] and by Yabroff, Branch and Bettman (m. p. 102°).[7] The dry acid oxidizes very rapidly in the air and must be manipulated in an inert atmosphere. Unlike the simple aliphatic boronic acids, this acid undergoes autoöxidation even in the presence of water.

Yabroff, Branch and Bettman[7] have reported that dry "benzylboric acid" is oxidized in air to benzaldehyde. We have observed that slow autoöxidation in the presence of water produced benzyl alcohol. A sample of the boronic acid was dissolved in water and placed in a loosely corked flask filled originally with pure nitrogen. Air diffused slowly into the tube and at the end of five days oily drops had separated on the surface of the solution. These were removed, and on purification were found to consist chiefly of benzyl alcohol, b. p. 200–205°; benzoate, m. p. 16–18.5°.

Samples of the boronic acid were refluxed for three hours with boiled distilled water, 1% aqueous boric acid, and 5% aqueous sulfuric acid, but in no case was there evidence of appreciable hydrolysis. A sample of 1.77 g. of the boronic acid was dissolved in 50 cc. of 5% sodium hydroxide solution and subjected to gentle distillation. After seven minutes the toluene layer of the distillate amounted to 1.5 cc., indicating an essentially quantitative hydrolysis to toluene and boric acid.

**Reaction with Ammoniacal Silver Oxide.**—Qualitative experiments showed that α-tolueneboronic acid reduces ammoniacal silver oxide with the production of metallic silver and dibenzyl. Quantitative experiments were carried out to establish the equation for the reaction.

(a) A sample of the boronic acid purified by successive recrystallizations from water and benzene was dried in a stream of pure nitrogen and dissolved in boiled distilled water. The solution was titrated with carbonate-free sodium hydroxide in the presence of mannitol and found to be 0.0892 molar. A solution of ammoniacal silver oxide prepared from 50 cc. of 0.1 *N* silver nitrate was treated with 25 cc. of the boronic acid solution (2.23 millimoles). A black precipitate of silver formed immediately, but the mixture was warmed and shaken for ten to fifteen minutes to ensure complete reaction. The metallic silver was filtered, washed with dilute ammonia and water, dissolved in 20% nitric acid and titrated against standard ammonium thiocyanate. This determination was checked by titrating the excess of silver in the filtrate from the reaction. $RB(OH)_2$, 2.23 millimoles: Ag (from filtrate) 2.13, (ppt.) 2.13. These data show that 1 mole of the boronic acid reduced 0.965 mole of ammoniacal silver oxide to form 0.965 gram atom of silver.

(b) A sample of the pure boronic acid weighing 2.52 g. (18.5 millimoles) was added to a solution of ammoniacal silver oxide prepared from 5.0 g. of silver nitrate. The flask was fitted with a reflux condenser, warmed at 70° for twenty minutes, then brought to boiling and filtered. The silver was washed carefully with dilute aqueous ammonia, water, methanol and ether. It was then dissolved in 20% nitric acid, and an aliquot portion of the solution was titrated with ammonium thiocyanate: Ag ppt. = 152.9 cc. 0.1 *N* $NH_4SCN$ = 15.3 milli-atoms Ag. The filtrate was extracted with 60–70° ligroin in a small continuous extractor for six hours and gave 1.31 g. (7.2 millimoles, 94% of the theoretical) of crude dibenzyl. The dibenzyl distilled at 278–280°, and after one recrystallization from ethanol melted at 51–52.5°.

**2-Methylpropane-2-boronic Acid ("*t*-Butylboric Acid").**—This acid was prepared in the usual way, from *t*-butylmagnesium chloride and methyl borate, in 50–60% yields. Since the acid sublimes and steam distils readily, care must be taken to avoid losses by volatilization. The dry acid oxidizes with great rapidity in the air. Samples recrystallized from water or toluene melted at 103–105°, with decomposition. This boronic acid has been prepared previously by Krause and Nobbe,[11] by the slow autoöxidation of tri-*t*-butylborine and subsequent hydrolysis, and described as a volatile, white crystalline solid, m. p. 113°.

The ease with which this boronic acid undergoes oxidation made quantitative experimental work very difficult. However, the anhydride of the acid, *t*-butylboron oxide, could be manipulated without exposure to air, and by careful hydration of weighed samples of the oxide in air-free water and in an atmosphere of nitrogen it was possible to obtain solutions containing a known quantity of the pure boronic acid.

*t*-Butylboron oxide was prepared by treating the acid with thionyl chloride; it is a colorless liquid, b. p. 66–68° (5 mm.), which crystallizes on cooling and melts at about 20°.

*Anal.* Calcd. for $C_4H_9BO$: B, 12.90. Found: B, 13.00.

This boronic acid, like the *n*-butyl and *n*-hexyl analogs, is too weak an acid to permit titration with alkali in the presence of mannitol: neut. equiv. calcd., 101.9; found (sample prepared from the oxide), 122.

**Reaction with Ammoniacal Silver Oxide.**—(a) Quantitative experiments were carried out as described for α-tolueneboronic acid, using samples prepared from *t*-butylboron oxide. One mole of the acid produced 1.89–1.90 gram atoms of silver: $RB(OH)_2$, 2.30 millimoles; Ag, 4.34. (b) A solution of the boronic acid prepared from 4.474 g. (53.4 millimoles) of *t*-butylboron oxide was treated with ammoniacal silver oxide prepared from 18.53 g. (109.0 millimoles) silver nitrate and 2% aqueous ammonia. Although the solutions were mixed at 0°, a black precipitate of silver formed at once. The mixture was heated at 60–70° for one-half hour and then refluxed for ten minutes. A trap (cooled in liquid air) at the head of the condenser collected a small amount (0.3 g.) of low-boiling liquid,

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(9) Khotinsky and Melamed, *Ber.*, **42**, 3094 (1909).

(10) Krause, German Patent 371,467 [*Friedländer*, **14**, 1450 (1924)].

(11) Krause and Nobbe, *Ber.*, **64**, 2112 (1931).

which on analysis was found to be a mixture of isobutane and isobutylene. The reaction mixture was distilled almost to dryness and the distillate salted out with potassium carbonate and extracted five times with ether. Fractionation gave 3.2 g. of crude *t*-butyl alcohol (b. p. 75–85°; $n^{25}_D$ 1.3862; α-naphthyl urethan, m. p. 98–100°) which is equivalent to 0.815 mole per mole of the boronic acid.

**2-Furanboronic Acid.**—2-Iodofuran, prepared from furoic acid by the method of Gilman, Mallory and Wright,[12] was converted into 2-furylmagnesium iodide in 87% yield. From 0.41 mole of this Grignard reagent and 44 g. (0.44 mole) of methyl borate there was obtained 32 g. (78% yield) of the boronic acid. This acid is fairly stable in the air, but discolors slowly on standing. It is slightly soluble in hot ligroin (b. p. 60–70°) and is very soluble in acetone, alcohol, and ether. It may be recrystallized from water, benzene, or toluene.

The acid forms fine, white crystals from water, which melt with decomposition at 110°. From benzene or toluene white lustrous flakes are obtained which melt sharply at 121–122°. Titration with alkali in the presence of mannitol showed that both specimens correspond to the anhydrous acid $C_4H_3O-B(OH)_2$: neut. equiv. calcd. 111.9; found, 111.8 (from water), 111.5 (from toluene).

**Reaction with Ammoniacal Silver Oxide.**—When 2-furanboronic acid is treated with aqueous silver nitrate in neutral or ammoniacal solution, a bright orange precipitate of the silver salt forms immediately. On warming, the precipitate decomposes and leaves a perfectly homogeneous solution with no evidence of any metallic silver. From 3.5 g. of the boronic acid, there was obtained 1.7 g. (80% of the theoretical amount) of furan which was identified by its refractive index ($n^{20}_D$ 1.4231), and maleic anhydride adduct (m. p. 123°, with dec.). The reaction is therefore an hydrolytic cleavage, analogous to that of the aromatic boronic acids.

**Replacement Reactions.** (a) **Mercuric Chloride.**—In aqueous solution at 25°, 2-furanboronic acid reacted rapidly with mercuric chloride to give a white precipitate of 2-chloromercurifuran. After recrystallization from 50% alcohol the product melted at 152–153° (reported, 151°).[13]

(b) **Cupric Halides.**—Ainley and Challenger[5] have shown that benzeneboronic acid reacts with cupric chloride or bromide with the formation of the cuprous halide and replacement of the boric acid residue by halogen. The aliphatic boronic acids do not react with cupric halides.

2-Furanboronic acid reacts very slowly with cupric chloride; after warming in aqueous solution for twelve hours very small amounts of cuprous chloride and 2-chlorofuran were formed. The reaction with cupric bromide is quite rapid and is exothermic. Within a few minutes the solution is decolorized and a heavy precipitate of cuprous bromide is formed. To a solution of 0.8 g. of 2-furanboronic acid in 6 cc. of water, 1.6 g. of cupric bromide was added and the flask was warmed gently until the color faded to a light blue. Solid potassium cyanide was added to dissolve the cuprous bromide and the 2-bromofuran was extracted with ether. The extract was dried over calcium chloride, filtered, and treated with 0.7 g. of maleic anhydride. After standing for fifteen hours the resulting precipitate of the maleic anhydride adduct was filtered. The product weighed 0.5 g. (28% yield) and, after crystallization from ether, melted at 114–115° with dec. The reported m. p. of the maleic anhydride adduct of 2-bromofuran is 116°, with dec.[14]

(c) **Iodinating Agents.**—When 2-furanboronic acid was treated with a solution of iodine in aqueous potassium iodide (1.3 g. of iodine and 2.5 g. of potassium iodide in 10 cc. of solution), the iodine color was discharged slowly and 2-iodofuran was formed. A similar reaction occurred when the boronic acid was dissolved in cold 5% potassium hydroxide and small crystals of iodine were added to the solution. In both cases the 2-iodofuran was extracted with ether and identified by means of the maleic anhydride adduct, m. p. 118–119°.

**2-Thiopheneboronic Acid.**—2-Iodothiophene was prepared from synthetic thiophene by iodination in the presence of mercuric oxide,[15] and converted into 2-thienylmagnesium iodide (in an atmosphere of dry nitrogen). From 0.28 mole of the Grignard reagent and 49 g. (0.47 mole) of methyl borate there was obtained 35 g. (95% yield) of the crude boronic acid, m. p. 130–135°. Two crystallizations from water, followed by drying in air, gave white crystals which melted at 134–135° without effervescence or decomposition. Samples recrystallized from benzene melted at 133–134°. The acid formed pure white, odorless crystals which melted sharply, resolidified on cooling, and remelted at the original melting point.

This acid has been prepared previously by Krause and Pomeranz[16] who obtained it from 2-thienylmagnesium bromide and boron trifluoride. They state that the boronic acid separated as a monohydrate, m. p. 134°, but our results indicate clearly that the white crystalline solid obtained from water or hydrocarbon solvents is the anhydrous acid. Samples were purified by crystallization from hot water, and by crystallization from water followed by crystallization from toluene. Both specimens melted at 133–134° without decomposition, and titration with carbonate-free alkali in the presence of mannitol (phenolphthalein indicator) gave neutralization equivalents checking the value for the anhydrous acid. Neut. equiv.: found, 127.3 (from water), 128.6 (from water, followed by toluene); calcd. for the anhydrous acid, 127.9, for the monohydrate, 145.9.

2-Thiopheneboronic acid readily undergoes hydrolytic cleavage on warming to 50–60° with 6 *N* hydrochloric acid, or by refluxing gently with 20% aqueous sodium hydroxide. In both experiments the resulting thiophene was identified by conversion to 2-chloromercurithiophene, m. p. 181–182° (reported m. p. 183°).

**Reaction with Ammoniacal Silver Oxide.**—A pale yellow precipitate of the silver salt was formed when an aqueous solution of the boronic acid was treated with aqueous silver nitrate. The precipitate decomposed into thiophene on warming, leaving a perfectly clear solution with no trace of metallic silver. The thiophene was removed by steam distillation and identified by mercuration. From 2.3 g. of 2-thiopheneboronic acid there was obtained 1.1 g. of thiophene (73% of the theoretical), which was mercurated

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[12] Gilman, Mallory and Wright, This Journal, **54**, 734 (1932).

[13] Gilman and Wright, *ibid.*, **55**, 3302 (1933).

[14] Van Campen and Johnson, *ibid.*, **55**, 430 (1933).

[15] Minnis, *Org. Syntheses*, **12**, 44 (1932).

[16] Krause and Pomeranz, *Ber.*, **65**, 777 (1932).

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.

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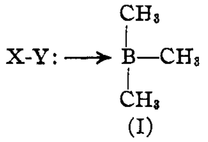
[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

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

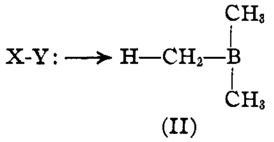
BY JOHN R. JOHNSON, H. R. SNYDER AND M. G. VAN CAMPEN, JR.[2]

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.



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

(I)



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

(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).