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

Organoboron Compounds, and the Study of Reaction Mechanisms. Primary Aliphatic Boronic Acids[1]

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In the development of current electronic theories of organic reactions, molecules are considered to react by virtue of a constitutional affinity either for electrons or for atomic nuclei. As a convenient expression of the behavior of their active centers relative to other systems, reagents have been classified by Robinson[2] and Ingold[3] as electron-accepting (cationoid or electrophilic) and electron-donating (anionoid or nucleophilic). In general the formal classification of a reactive molecule, atom, or ion, has been based upon considerations of the over-all transition from the initial to the final state and is independent of specific hypotheses concerning the intimate electronic mechanism of the reaction. From the standpoint of reaction mechanisms the mere recognition of the type of electroaffinity of the active centers is not sufficient; an electron-seeking reagent may react by the direct acquisition of electrons, or it may acquire additional electrons (or a larger share in the electrons of a covalent bond) by indirect means involving a temporary electron depletion.

There is evidence to support the view that many typical reactions are initiated by the formation of unstable coördination complexes,[4] in which the mobile electronic shell of the coördination center facilitates a close approach of covalent systems in a highly active condition. At present very little is known of the factors governing the formation of these reactive complexes or the nature of the transpositions that occur within them. In some instances analogies may be drawn from the known behavior of relatively stable inorganic complexes, but the more significant examples are frequently complexes for which no stable analogs are known. Further difficulties arise from the circumstance that many organic and inorganic molecules (or ions) are potentially bifunctional with respect to coördination processes; that is, a given molecule is capable of functioning either as an electron donor or acceptor, or of presenting two different points of attack for an external donor or acceptor center.

In the current electronic interpretation of typical organic reactions, intimate mechanisms have been postulated in which an unstable configuration of six electrons (open-sextet) is regarded as the driving force of the reaction.[5] Since these fugitive intermediates cannot be isolated and examined independently, the validity of these theories cannot be tested directly. However, organic derivatives of 3-covalent boron afford examples of structures containing an open-sextet of electrons and offer a means of studying the behavior of a simple acceptor (nucleophilic) center toward typical chemical reagents. Owing to the close relationship of boron and carbon, in so far as effective nuclear charge and atomic radius are concerned, one may expect studies of organoboron compounds to be of value in interpreting the behavior of analogous electronic systems associated with carbon.

Since organic derivatives of boron, especially in the aliphatic series, have not been studied extensively it seemed desirable to undertake a systematic investigation in this field. Preliminary preparative work and orienting experiments dealing with a group of primary aliphatic boronic acids, $RB(OH)_2$, are reported in the present paper. Succeeding papers will deal with other types of boronic acids, with derivatives of the borinic acids $R_2B{-}OH$, and with the borines R_3B.[6]

A number of aromatic boronic acids of the type $Ar{-}B(OH)_2$ have been described and they are found to take part readily in a variety of replacement reactions. Only a few representatives of the aliphatic boronic acids have been reported and little is known of their chemical behavior. Frankland,[7] who first prepared organoboron compounds, obtained ethaneboronic acid by the hy-

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(1) This report is part of a paper on organoboron compounds which was presented at the Sixth Organic Chemistry Symposium, Rochester, New York, December, 1935.

(2) Robinson, "Outline of an Electrochemical (Electronic) Theory of the Course of Organic Reactions," Institute of Chemistry of Great Britain and Ireland, London, 1932.

(3) Ingold, *J. Chem. Soc.*, 1120 (1933); *Chem. Rev.*, **15**, 225 (1934).

(4) Meerwein, *Ann.*, **455**, 227 (1927); Carothers and Berchet, THIS JOURNAL, **55**, 2809 (1933); Johnson, *ibid.*, **55**, 3029 (1933).

(5) Carothers, *ibid.*, **46**, 2226 (1924); Whitmore, *ibid.*, **54**, 3274 (1932); see also, Bartlett and Pöckel, *ibid.*, **59**, 821 (1937).

(6) In conformity with suggestions of Dr. Austin M. Patterson the three principal series of organoboron compounds, $R{-}B(OH)_2$, $R_2B{-}OH$ and R_3B, are designated respectively: alkaneboronic acids (instead of "alkylboric acids"), dialkylborinic acids (instead of "dialkylboric acids"), and trialkylborines (instead of "trialkylborons"). An authoritative system of nomenclature for organoboron compounds has not yet been adopted.

(7) Frankland, *J. Chem. Soc.*, **15**, 363 (1862).

drolysis of its diethyl ester, $C_2H_5B(OC_2H_5)_2$, produced by the slow oxidation of triethylborine. The controlled oxidation of trialkylborines is evidently a general method of preparation for the aliphatic boronic acids and was employed subsequently by Krause[8] and his collaborators to obtain the *n*-propyl, isobutyl, *t*-butyl and isoamyl compounds. Khotinsky and Melamed[9] found that aliphatic and aromatic boronic acids can be prepared readily by the action of Grignard reagents upon alkyl esters of boric acid, and more recently Krause[10] has employed the etherate of boron trifluoride instead of an alkyl borate. Our experience indicates that the method of Khotinsky and Melamed, with slight modification, is the most convenient general procedure for the preparation of primary aliphatic boronic acids.[11]

There is a rather striking lack of agreement in the melting points of aliphatic boronic acids reported by different investigators. These discrepancies appear to be due, apart from minor differences in melting point technique, to the difficulty of obtaining specimens of aliphatic boronic acids that actually correspond to the formula $R-B(OH)_2$. The acids frequently separate from aqueous solutions as hydrates, and the latter on standing in a desiccator over the usual drying agents pass through the stage of the anhydrous acids $R-B(OH)_2$ and finally yield alkylboron oxides of the composition R–BO. Furthermore, dry samples of the aliphatic boronic acids undergo atmospheric oxidation to give a product contaminated with boric acid. After preliminary trials it was found that anhydrous aliphatic boronic acids corresponding to the formula $R-B(OH)_2$ could be obtained by drying purified samples over 65% sulfuric acid in an atmosphere of nitrogen. 1-Butaneboronic acid after drying in this way corresponded in composition and molecular weight to the formula $C_4H_9B(OH)_2$.

1-Butane- and 1-hexaneboronic acids were chosen as appropriate compounds for detailed study. They are extremely weak acids and, unlike boric acid and the benzeneboronic acids, are not rendered sufficiently acid by the addition of mannitol to enable titration against standard alkali.[12] With very concentrated sodium hydroxide 1-butaneboronic acid gave a hydrated sodium salt, which upon pyrolysis gave *n*-butane. Prolonged heating with strong aqueous alkalies, or with 40% hydrobromic or hydriodic acid, does not effect hydrolytic cleavage of the boron–carbon linkage.

Ainley and Challenger[13] have shown that aromatic boronic acids undergo a facile cleavage of the boron–carbon bond upon warming with aqueous solutions of various metallic salts (mercuric, cadmium, zinc and cupric halides). The typical aryl compounds do not undergo atmospheric oxidation but are cleaved by aqueous hydrogen peroxide[13] or bromine water. The primary aliphatic boronic acids proved to be inert toward all of these reagents (in aqueous solutions at 100°)[14] except hydrogen peroxide, and to be quite susceptible to atmospheric oxidation. Hydrogen peroxide, especially in the presence of dilute alkali, effects a quantitative oxidation to give the alcohol and boric acid. This reaction

$$n\text{-}C_4H_9\text{-}B(OH)_2 + H_2O_2 \longrightarrow n\text{-}C_4H_9OH + H_3BO_3$$

and the thermal decomposition of the sodium salts, are the only examples in which the aryl and primary aliphatic boronic acids were found to behave in the same way.

It was observed by earlier investigators[8,9] that aliphatic boronic acids reduce silver nitrate readily in ammoniacal solution but the nature of the organic product had not been determined. A quantitative study of this reaction, with 1-butane- and 1-hexaneboronic acids, showed that the quantity of metallic silver produced corresponds to 0.95-1.0 gram atom per mole of the boronic acid and that the hydrocarbon R–R is formed. From 1-butaneboronic acid, 70–80% of the theoretical amount of *n*-octane was isolated and no other organic product was detected. This behavior is in marked contrast to an arylboronic acid, which yields the hydrocarbon RH under these conditions.[15]

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

The boronic acids may be converted to alkyl-

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[8] Krause and Nitsche, *Ber.*, **54**, 2784 (1921); Krause and Nobbe, *ibid.*, **64**, 2112 (1931).

[9] Khotinsky and Melamed, *ibid.*, **42**, 3094 (1909). Organomercurials had been used earlier by Michaelis and Becker, *Ber.*, **15**, 182 (1882).

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

[11] Subsequent work of Dr. M. G. Van Campen and Dr. Oliver Grummitt in This Laboratory has shown that organoboronic acids containing secondary and tertiary alkyl and cycloalkyl groups may be prepared in satisfactory yields by this method.

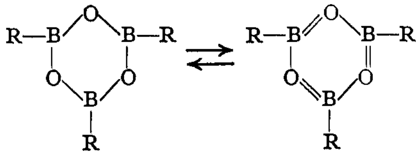
[12] Branch, Yabroff and Bettman, THIS JOURNAL, **56**, 937, 1850 (1934).

[13] Ainley and Challenger, *J. Chem. Soc.*, 2171 (1930).

[14] Challenger and Richards [*ibid.*, 410 (1934)] have reported that *n*-propaneboronic acid on heating with aqueous mercuric chloride for twenty hours at 140–150° gave a 55% yield of *n*-propylmercuric chloride.

[15] Seaman and Johnson, THIS JOURNAL, **53**, 711 (1931).

boron oxides by drying over concentrated sulfuric acid or phosphorus pentoxide, at room temperature. The oxides are obtained also by heating the acids, gently under reduced pressure, or by treatment with thionyl chloride. The oxides of the *n*-butyl and *n*-hexyl compounds are colorless liquids which distill without decomposition under reduced pressure and regenerate the acids upon treatment with water. They have the composition R–BO but molecular weight determinations show them to be trimeric. The fact that they are definite trimers[16] indicates a cyclic structure analogous to that of the trimeric aliphatic aldehydes, and this view is confirmed by the observation that the boiling point of *n*-butylboron oxide is close to that of the corresponding paraldehyde homolog. The relatively great stability of the cyclic trimers may be due in part to resonance effects involving an unshared electron pair of the oxygen atom and the open sextet of 3-covalent boron.



Trimeric Alkylboron Oxide

In several respects the primary aliphatic boronic acids show a superficial resemblance to aliphatic aldehydes; the boronic acids combine with molecular oxygen, reduce ammoniacal silver oxide to metallic silver, and undergo cyclization to a six-membered ring structure. Possibly the similarity of the boronic acids and aldehydes may be attributed to the presence of analogous electronic configurations. The organoboron compound contains an open sextet of electrons, and is similar to the active form of the aldehyde in this respect. In both cases the initiation of reaction can be considered to be due to the acceptor activity of the deficient atom.

The experiments reported here show that the primary aliphatic boronic acids differ sharply from aromatic boronic acids in chemical behavior. Studies of organoboronic acids containing secondary and tertiary alkyl groups and cycloalkyl groups, are now in progress and have indicated that these types behave quite differently from the primary aliphatic boronic acids.

Experimental

1-Butaneboronic Acid.—This acid was prepared by the following general procedure which was used without essential modification for all of the boronic acids studied. A 1-liter three-necked flask was fitted with an efficient mercury-sealed stirrer, and one neck was provided with a low temperature thermometer and a glass tube for the introduction of nitrogen. The remaining neck carried a 500-cc. separatory funnel and an outlet tube for nitrogen. Clean corks were used in all the fittings. The nitrogen outlet tube and the top of the separatory funnel were connected to two arms of a Y-tube, the third arm of which was sealed by a mercury valve. The stem of the separatory funnel was bent so that the liquid would be introduced near the center of the flask.

Dry nitrogen, purified over sulfuric acid and alkaline pyrogallol, was allowed to flow through the apparatus for twenty minutes. Then 55 g. (0.53 mole) of *pure* methyl borate was added quickly through the separatory funnel and washed through with 150 cc. of anhydrous ether. The flask was suspended in a Dewar dish containing a mixture of acetone and solid carbon dioxide and the solution was stirred during the cooling. When the internal temperature had fallen to about −75°, 300 cc. (0.50 mole) of *n*-butylmagnesium bromide solution (1.66 *N*) was introduced slowly through the separatory funnel over a period of about six hours. The flow of nitrogen and vigorous stirring were maintained during the addition and the temperature was kept below −70°. During the addition a voluminous precipitate separated; when the addition was complete the mixture was stirred at −70° for four hours longer and then allowed to stand in the cooling bath overnight. At the end of this time it had warmed up to −10°, and consisted of a heavy precipitate covered by a clear liquid. The flask was opened momentarily and the cake of precipitate broken into small lumps with a glass rod. The apparatus was reassembled and 300 cc. of water containing 30 cc. of sulfuric acid was added with stirring and cooling. No appreciable amount of heat was evolved during this hydrolysis.

The ethereal layer was separated and the aqueous layer was extracted with 50 cc. of ether, which was combined with the main portion. The ethereal solution was concentrated on a steam-bath, 20 cc. of water was added, and the distillation continued until all material volatile at the temperature of the steam-bath was removed. The crystalline acid, which separated upon cooling the residual liquid, was filtered with suction and the moist crystals were placed in a nitrogen-filled desiccator over 65% sulfuric acid (sp. gr. 1.55). The crude acid weighed 30–35 g. (60–70% yield).

The crude acid was warmed with 275 cc. of toluene, the solution filtered at 60° and chilled thoroughly. The purified acid was washed with 25 cc. of cold toluene, followed by two 25-cc. portions of redistilled petroleum ether (b. p. 30–50°) and stored in a nitrogen-filled container. The purified acid weighed 25–26 g. (50% yield). It usually proved convenient to store the acids in the crude moist condition, or merely to store the moist ethereal extract, and to purify specimens as needed. The dry purified samples must be excluded from contact with air, but moist specimens do not suffer autoöxidation.

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[16] Kinney and Pontz [THIS JOURNAL, **58**, 197 (1936)] have shown recently that the crystalline arylboron oxides are also trimeric and have formulated them as cyclic structures.

Good yields in these preparations depend largely upon efficient stirring and maintenance of the low temperature (−70°). At −10° the yields fell to 10–12% of the theoretical. In one preparation (at −70°) the Grignard reagent was introduced near the side of the flask, causing the deposition of a precipitate which interfered with stirring, and the yield was only 30%. When *n*-butyl borate was used instead of methyl borate the yields were also lower (25%).

Even the purest specimens of 1-butaneboronic acid did not show a sharp melting point. When the temperature was raised at the rate of 1° per minute, the acid melted at 92–94° (previously reported, 93–94°). During fusion a slow effervescence occurred, which became vigorous above 100°; samples which had undergone vigorous effervescence did not resolidify on cooling, but those which had been heated less strongly resolidified and melted again at 92–94°. Analysis for carbon and hydrogen was carried out by the semi-micro combustion method. It is essential that combustion take place exclusively over the catalyst; when ignition took place in the boat, or flashing occurred, the results were unsatisfactory. Boron was determined by conversion to boric acid, using sodium peroxide or aqueous hydrogen peroxide (see below), and titration in the presence of mannitol. The molecular weight was determined by the boiling point rise in acetone.

Anal. Calcd. for $C_4H_{11}O_2B$: C, 47.10; H, 10.88; B, 10.62; mol. wt., 102.0. Found: C, 47.04, 47.02; H, 10.93, 11.03; B, 10.50, 10.56; mol. wt., 102.1, 103.1.

1-Butaneboronic acid is readily soluble in ether, alcohol, chloroform, acetone, ethyl acetate, and glacial acetic acid. It is less soluble in water, benzene, toluene, carbon tetrachloride, ethylene dichloride, or petroleum ether, and may be recrystallized from these solvents. The acid dissolves readily in 40% aqueous hydrofluoric acid, and in 10% sodium hydroxide solution. The aqueous solution of the acid is neutral to litmus, and even in the presence of mannitol cannot be titrated satisfactorily with standard alkali (phenolphthalein). On standing in a desiccator over concd. sulfuric acid or phosphorus pentoxide the crystalline solid passes into the liquid anhydride (see below).

The acid was not affected by heating for several hours with iodine in aqueous potassium iodide, or 48% hydrobromic acid, or aqueous solutions of mercuric chloride, bromide or acetate. It reacts readily with aqueous hydrogen peroxide and with ammoniacal silver oxide.

Sodium Salt.—One gram of the pure acid was dissolved in 3 cc. of 20% sodium hydroxide and saturated sodium hydroxide solution added as long as a precipitate formed. The crystals were filtered in a sintered glass funnel, dissolved in 10 cc. of absolute alcohol and reprecipitated by addition of 100 cc. of purified acetone. The crystals were washed copiously with acetone, finally with dry ether, and spread out in the air to remove ether (weight, 1.1 g.). The salt did not undergo autoöxidation in the air. It dissolved readily in water to give a strongly alkaline solution, and the sodium content was determined by titrating with standard acid in the presence of methyl red. Air-dried specimens obtained as described above corresponded to a hydrate of the formula $Na[C_4H_9BO_2H + {}^1/_2H_2O]$: calcd. Na, 17.32; found, 17.46, 17.50. After drying over phosphorus pentoxide, the material corresponded to an anhydrous salt, $Na_2[(C_4H_9BO)_2O]$.

One gram of the air-dried salt was heated in a small distilling flask over a free flame. A few drops of water distilled at first and then *n*-butane was evolved. The gas did not dissolve in cold concd. sulfuric acid, and on cooling condensed to a colorless liquid which boiled at 0°.

Autoöxidation.—Dry specimens of the pure acid are oxidized slowly by air with the formation of *n*-butyl alcohol and boric acid. Tests for aldehydes with Schiff's reagent were negative. The reaction is evidently an oxidation of the anhydrous acid, *followed* by slow hydrolysis of the initial product.

$$2C_4H_9B(OH)_2 + O_2 \longrightarrow 2C_4H_9O{-}B(OH)_2$$

$$C_4H_9O{-}B(OH)_2 + H_2O \longrightarrow C_4H_9OH + H_3BO_3$$

The inhibiting action of water was shown in the following way. A small sample (0.3 g.) of the pure anhydrous acid was placed in an inverted graduated tube over mercury in an atmosphere of dry oxygen. The volume of oxygen decreased slowly and no appreciable contraction occurred during the first day; 1.5 cc. was consumed during the second day, 4.6 cc. the third day, 14.4 cc. the fourth day, and all of the remainder (4 cc.) during the fifth day. In a parallel experiment two drops of water were added to the sample before exposure to oxygen, and in this case no oxygen was taken up during a period of eighteen months.

Oxidation by Hydrogen Peroxide.—One gram of the acid was heated for five minutes with 20 cc. of 30% hydrogen peroxide solution. The cooled solution upon extraction with ether gave 0.7 cc. of *n*-butyl alcohol, which was identified through the 3,5-dinitrobenzoate, m. p. 62°.

Reaction with Ammoniacal Silver Oxide.—Five grams of the pure anhydrous acid was added to ammoniacal silver oxide prepared by dissolving 8.5 g. of silver nitrate in 50 cc. of water and adding 10% aqueous ammonia until the precipitated oxide redissolved. The flask was warmed gently under reflux and at about 70° the separation of metallic silver began. The mixture was boiled gently for ten minutes and then distilled. From the distillate there was obtained 2.0 g. (70% of the theoretical amount) of *n*-octane; b. p. 124–125°, $n^{22}D$ 1.3987. The hydrocarbon did not react with sodium, concd. sulfuric acid, bromine in carbon tetrachloride, or alkaline permanganate solution. The amount of metallic silver formed corresponded to 1 gram atom per mole of the boronic acid.

***n*-Butylboron Oxide (1-Butaneboronic Anhydride).**—In a 25-cc. modified Claisen flask provided with a small side-tube condenser and a device for collecting fractions without interruption, was placed 10 g. of pure 1-butaneboronic acid. Dry nitrogen was admitted through the capillary tube, and the flask was evacuated with a water-pump and heated on a steam-bath. Sublimation and steam distillation of the acid caused some difficulty. When no further distillation occurred the flask was heated in an oil-bath. There was obtained 4.0 g. (50% yield) of the oxide, b. p. 138° (18 mm.). The unchanged acid was recovered practically quantitatively from the aqueous forerun.

The oxide was redistilled in nitrogen (b. p. 136° at 16 mm.) and sealed in small bulbs for analysis. Carbon and hydrogen were determined by the semi-micro method, and the molecular weight by the ebullioscopic method in benzene.

Anal. Calcd. for C_4H_9BO: C, 57.22; H, 10.82. Found: C, 57.59, 57.33; H, 10.92, 10.70. *Mol. Wt.* Calcd. for C_4H_9BO, 83.9; for $(C_4H_9BO)_3$, 251.7. Found: 262.6 (mean).

The oxide is prepared more conveniently by warming the acid with thionyl chloride. To 9.0 g. (0.09 mole) of 1-butaneboronic acid was added 33 g. (20 cc., 0.27 mole) of pure thionyl chloride. Gas was evolved and the mixture became quite cold. When the spontaneous reaction slackened the mixture was warmed gently and finally refluxed for an hour. The reaction mixture was distilled in a nitrogen atmosphere under reduced pressure. After removal of the excess thionyl chloride there was obtained 6.1 g. (80% yield) of the anhydride, b. p. 154° (30 mm.).

n-Butylboron oxide is a colorless liquid that reacts with water, with slight evolution of heat, to regenerate the acid, m. p. 92–94°. When anhydrous ammonia was bubbled into a solution of the oxide in dry ether, a white crystalline precipitate was formed. Heat was generated when the oxide was added to phenylhydrazine, aniline, methylaniline, dimethylaniline, diethylamine, triethylamine, di-*n*-butylamine, and tri-*n*-butylamine, but a solid compound was not obtained in any case. Heat was generated when the oxide was added to absolute methanol or ethanol.

Treatment of an ethereal solution of the anhydride at −65° with a considerable excess of *n*-butylmagnesium bromide (3 moles) gave a small quantity of tri-*n*-butylborine, but most of the material was recovered after hydrolysis as 1-butaneboronic acid.

1-Hexaneboronic Acid.[17]—Pure *n*-hexyl bromide (b. p. 155–157°, n^{20}_D 1.4485) was converted to the Grignard reagent (yield 93%, by titration). A solution containing 0.57 mole of the latter was added to 60 g. (0.54 mole) of pure methyl borate at −75°, following the general procedure given above. The yield of crude moist acid was 42–43 g. (70% of the theoretical).

Crystallization from water, then from ethylene dichloride, gave pure white crystals, m. p. 88–90°.

Anal. Calcd. for $C_6H_{15}O_2B$: B, 8.33. Found: B, 8.39, 8.34.

The acid is sparingly soluble in water and has a neutral reaction to litmus. Like the *n*-butyl compound, it does not develop sufficient acidity when mannitol is added, to permit titration with sodium hydroxide in the presence of phenolphthalein. An indefinite color change occurs before one equivalent of alkali has been added: neut. equiv., calcd. 130; found, 176, 160.

On warming with 30% hydrogen peroxide solution the acid yielded boric acid and *n*-hexyl alcohol. The latter was identified as the 3,5-dinitrobenzoate, m. p. 58.5° (reported, 58.4°).

When the acid is warmed with faintly ammoniacal silver nitrate solution, metallic silver is precipitated. Quantitative experiments in which the reaction mixture was refluxed gently for thirty minutes, gave the following ratios of $Ag/RB(OH)_2$: 0.99, 0.99, 0.97. The values were checked by determination of the precipitated silver, and the excess of silver in the filtrate. In one experiment the reaction mixture was distilled and the organic product isolated from the distillate; from 3.58 g. (27.5 millimoles) of the acid and 5.82 g. (34.3 millimoles) of ammoniacal silver nitrate there was obtained 1.98 g. (11.6 millimoles, 85% of the theoretical) of *n*-dodecane; b. p. 205–218°, n^{25}_D 1.4185, d^{25}_4 0.750. The hydrocarbon did not decolorize bromine water or alkaline permanganate. Physical constants reported for *n*-dodecane are:[18] b. p. 216.2°, n^{25}_D 1.41967, d^{25}_4 0.74542.

The crystalline acid is converted to the liquid anhydride on standing in a desiccator over concd. sulfuric acid or phosphorus pentoxide. On slow heating under reduced pressure, followed by distillation, 13 g. of the acid gave 8.6 g. (75% yield) of *n*-hexylboron oxide; colorless liquid, b. p. 149–151° (4 mm.), 178–182 (24 mm.), n^{20}_D 1.4323, d^{20}_4 0.8876. The oxide was also prepared by refluxing the acid for one hour with an excess (3 moles) of thionyl chloride. On contact with water the oxide regenerates the boronic acid with slight evolution of heat.

Anal. Calcd. for $(C_6H_{13}BO)_3$: B, 9.67. Found: B, 9.35, 9.25.

1-Pentaneboronic Acid.[17]—*n*-Amyl bromide (b. p. 54–56° (55 mm.), n^{20}_D 1.4440) was converted to the Grignard reagent, and the reaction with methyl borate was carried out in the usual way. From 0.5 mole of the Grignard reagent and 53.5 g. (0.52 mole) of methyl borate there was obtained 40 g. of the crude, moist acid (70% yield). Crystallization from water, then from ethylene dichloride, gave heavy, white flakes; m. p. 93–94°.

Anal. Calcd. for $C_5H_{13}O_2B$: B, 9.33. Found: B, 9.33, 9.35.

One gram of the acid was refluxed with 20 cc. of 30% hydrogen peroxide and gave 0.7 cc. of *n*-amyl alcohol; 3,5-dinitrobenzoate, m. p. 46.3° (reported, 46.4°).

1-Propaneboronic Acid.[17]—The addition of 0.5 mole of *n*-propylmagnesium bromide to 54.5 g. (0.52 mole) of methyl borate, in the usual way, gave 24.5 g. (54% yield) of the crude moist acid. Difficulty was experienced in purifying this product; repeated crystallizations from various solvents, and sublimation, gave white crystals which melted at 105–110°. Another specimen purified by steam distillation, recrystallization from water and from ethylene dichloride, and dried over 65% sulfuric acid, melted at 106–107°. Previous investigators have reported 74, 106, and 112°.

2 - Methylpropane - 1 - boronic Acid ("Isobutylboric Acid").[17]—The Grignard reagent (0.54 mole) prepared from carefully purified isobutyl bromide (b. p. 90–92°, n^{20}_D 1.4361) was added to 57.5 g. (0.55 mole) of methyl borate in the usual way. The yield of crude, moist acid was 31.5 g. (57%). Even after crystallization from water and from ethylene dichloride the acid showed a wide melting range, 106–112°. Previous investigators have reported 104 and 112°. This acid appears to undergo autoöxidation much more rapidly than the *n*-butyl and *n*-hexyl compounds.

Anal. Calcd. for $C_4H_{11}O_2B$: B, 10.62. Found: B, 10.70, 10.57.

Oxidation of the acid with 30% hydrogen peroxide gave isobutyl alcohol; 3,5-dinitrobenzoate, m. p. 85° (reported, 86.5°).

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(17) A number of experiments with 1-hexane-, 1-pentane-, 1-propane-, and 2-methylpropane-1-boronic acids which are reported in this paper were carried out by Dr. Oliver Grummitt.

(18) Shepard, Henne, and Midgley, THIS JOURNAL, **53**, 1951 (1931).

1-Tetradecaneboronic Acid.—*n*-Tetradecanol, m. p. 38–38.3°, was converted to the bromide (b. p. 132–135° at 2 mm.). The Grignard reagent from this bromide was added to *n*-butyl borate and gave a crude, impure acid which was contaminated with the hydrocarbon $C_{28}H_{58}$. A large part of the latter was removed by dissolving the crude acid in 95% alcohol and chilling. The crystals which separated were identified as *n*-octacosane; m. p. 60–61.5°, mol. wt. (Rast), 377, 396. The boronic acid, obtained by evaporation of the alcohol and crystallization from petroleum ether, formed waxy crystals which melted over a wide range. A small specimen of the acid was oxidized by refluxing with 30% hydrogen peroxide, and gave *n*-tetradecanol, m. p. 38°.

Determination of Boron.—Two simplified procedures were developed for the determination of boron in organic combination. The essential processes in either method are oxidation of the organoboron compound to boric acid, and titration of the boric acid with alkali in the presence of mannitol.

Sodium Peroxide Method.—Fusion with sodium peroxide in the Parr bomb has been employed by Pflaum and Wenzke[19] in the analysis of compounds containing boron and fluorine. The following method was suggested by their procedure.

The weighed sample, sufficient to produce about 0.15 g. of boric acid, is introduced into a Parr bomb fusion cup containing 15 g. of sodium peroxide, 1 g. of potassium chlorate and 0.5 g. of sugar. The mixture is ignited with the usual precautions. After ignition the cup is placed in a 300-cc. R-glass beaker with 75–100 cc. of water. When the fusion mixture has dissolved completely the cup is withdrawn and rinsed, the rinsings being added to the contents of the beaker. The solution is cooled in ice and 6 *N* hydrochloric acid is added from a buret until evolution of carbon dioxide indicates that neutralization is almost complete. After adding 10 cc. of 10% sodium hydroxide, the solution is boiled to coagulate the metallic hydroxides from the fusion cup, and filtered into a 500-cc. round-bottomed R-glass flask equipped with a ground glass joint.

Two drops of methyl red solution are added, followed by 3 *N* hydrochloric acid until an excess of 3–5 cc. is present. During the addition of the acid the solution is cooled to prevent loss of boric acid by volatilization. The flask is fitted with a gas addition tube with glass joints to which a reflux condenser can be attached. The addition tube need not extend below the surface of the solution. A slow stream of nitrogen, purified by a sodium hydroxide tower, is passed through the apparatus while the solution is heated to reflux for fifteen to twenty minutes. The flask is then cooled without interrupting the flow of nitrogen. The condenser tube and the addition tube are rinsed thoroughly, the rinsings being added to the solution. A drop of methyl red is added to the solution and the flask is fitted with a rubber nipple which permits a flexible air-tight connection with a buret tip. The solution is roughly neutralized with 10% carbonate-free sodium hydroxide solution. It is adjusted to exact neutrality with 0.1 *N* solutions of sodium hydroxide and sulfuric acid. To the neutral solution are added three drops of phenolphthalein and 10 g. of mannitol. The nipple is replaced and the solution is titrated with 0.1 *N* carbonate-free sodium hydroxide, the first faint pink color of the phenolphthalein being taken as the end-point. During the titration the nipple is kept closed when possible to minimize atmospheric contact. It is necessary to open it occasionally to permit the escape of the air displaced by the added alkali. From the amount of alkali consumed between the methyl red and phenolphthalein end-points the percentage of boron in the sample is calculated.

The method gave satisfactory results with the boronic acids but is not suitable for the alkylborines, which ignite with great violence upon contact with sodium peroxide. The borines can be analyzed by the hydrogen peroxide method.

Hydrogen Peroxide Method.—This simpler method involves a milder form of oxidation and is particularly useful for the borines and certain other types which cannot safely be mixed with sodium peroxide. It is applicable also to the aliphatic boronic acids, and probably to all aliphatic boron compounds. Organic acids which may be formed in the peroxide oxidation are converted to carbonate by evaporating the alkaline mixture to dryness and igniting it.

A weighed sample of the boron compound roughly equivalent to 0.15 g. of boric acid, sealed in a small glass bulb if liquid, is introduced into a 25-cc. round-bottomed R-glass flask with ground glass joint. The flask is fitted with a ground glass addition tube carrying a 5-cc. dropping funnel, the stem of which is cut off just below the glass joint, and a small Allihn condenser. If the sample is a liquid the bulb is broken by shaking the apparatus. Through the addition tube 0.5 cc. of saturated sodium hydroxide solution is added, and while the apparatus is shaken 10 cc. of 5% hydrogen peroxide is added dropwise from the funnel. On completion of the addition the solution is warmed gently to decompose the peroxide, 1.5 cc. of saturated sodium hydroxide is then added, followed by the slow addition of 2–3 cc. of 30% hydrogen peroxide. During this addition the flask is warmed and shaken. The mixture is finally heated to reflux for about twenty minutes.

The flask is removed and its contents are transferred to a nickel crucible (40 × 45 mm.). The flask is washed with 5-cc. portions of water until the rinsings are neutral to litmus. The crucible is heated on the steam-bath for about two hours, after which the rate of evaporation becomes extremely slow. It is then heated on a sand-bath at 130–150° until the material solidifies. The crucible is removed from the sand-bath and heated very gently over a low flame until effervescence ceases. It is finally ignited to redness for about five minutes. After cooling it is placed in a 300-cc. R-glass beaker with 75 cc. of water. When the sodium hydroxide and salts have dissolved the crucible is removed and rinsed carefully. The solution is heated to boiling and filtered into a 500-cc. round-bottomed flask with a ground glass joint.

From this point the procedure is the same as that given in the second paragraph of the sodium peroxide method: two drops of methyl red solution are added followed by 3 *N* hydrochloric acid, etc. The hydrogen peroxide method has given excellent results with liquid compounds such as tri-*n*-butylborine and the alkylboron oxides.

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(19) Pflaum and Wenzke, *Ind. Eng. Chem., Anal. Ed.*, **4**, 392 (1932).

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 autooxidation 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.

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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.

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

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).