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Electrophilic Displacement Reactions. XIV. Two Novel Reactions Involving Areneboronic Acids and Halogens¹⁻³

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meta-Methoxybenzeneboronic acid has been found to react with one, two, and three moles of bromine to yield, respectively, 2-bromo-5-methoxybenzeneboronic acid, 2,4-dibromo-5-methoxybenzeneboronic acid, and 2,4,5-tribromoanisole. Chlorination yields 2-chloro-5-methoxybenzeneboronic acid and, probably, 3-methoxy-4-chlorobenzeneboronic acid. Reaction with iodine chloride yields 2-iodo-5-methoxybenzeneboronic acid along with the chloro acids.

Benzeneboronic acid reacts with hypochlorite and hypobromite to give phenol, which then reacts to form halophenols.

Halogenation of m-methoxybenzeneboronic acid. It has been known for some time that areneboronic acids suffer replacement of the boronic acid group on treatment with a number of reagents such as halogens,⁴ hydrogen peroxide,⁵ mercuric,⁵ and thallium salts.⁶ Hydrolysis occurs in water at 150° to yield benzene and boric acid; it is catalyzed by strong acid,⁵ strong base,⁵ and salts of cadmium,⁵ zinc,⁵ and silver.^{7,8} Because of this ease of replacement of the boronic acid group the acids have proved to be valuable in the study of aromatic electrophilic displacement reactions. A singular advantage lies in the fact that the seat of attack by the electrophilic reagent is generally known and difficulties attending the analysis of mixtures of isomers are eliminated. Exceptions to the rule that the boronic acid group is replaced in preference to hydrogen include the nitration of benzeneboronic acid^{5,9} to o- or m-nitrobenzeneboronic acid and the reaction of *m*-hydroxybenzeneboronic acid and *m*diethylaminobenzeneboronic acids with diazonium

(2) This research was supported by the Office of Naval Research and by the Directorate of Chemical Sciences, Air Force Office of Scientific Research. Taken in major part from the Master's theses of L. E. B., August 1954; A. D. P., August 1955; C. J. M., May 1957; and the doctoral dissertation of J. H. P., June 1960.

(3) A portion of this material was presented at the 130th Meeting of the American Chemical Society, Atlantic City, N. J., September 20, 1956; abstracts p. 58-O.

- (5) A. D. Ainley and F. Challenger, J. Chem. Soc., 2171 (1930).
- (6) F. Challenger and B. Parker, J. Chem. Soc., 1462 (1931).
 - (7) L. Michaelis and P. Becker, Ber., 15, 181 (1882).

(9) W. Seaman and J. R. Johnson, 53, 711 (1931).

salts.¹⁰ Coupling occurs *para* to the hydroxyl and diethylamino groups.

Another exception to the general rule has now been found in the reaction of *m*-methoxybenzeneboronic acid with halogens. When bromine was added to a solution of the boronic acid in 20%acetic acid, the color disappeared in a few seconds. On the basis of the effects of other substituents on the rate of the brominolysis reaction¹¹ it had been expected that the reaction would take days to go to completion. When this reaction was carried out on a synthetic scale with one molar equivalent of bromine, a new monobromoboronic acid was isolated in analytically pure state in 90% yield. It was hydrolyzed with aqueous zinc chloride to *p*-bromoanisole (92%). Thus the bromination product was 2-bromo-5-methoxybenzeneboronic acid, B-Br (Chart I).

The bromination was carried out with two moles of bromine per mole of *m*-methoxybenzeneboronic acid, yielding up to 90% of a dibromobenzeneboronic acid. This was characterized by oxidation with hydrogen peroxide to 2,4-dibromo-5-methoxyphenol, H—Br, as 2,4-dibromo-5-methoxybenzeneboronic acid, F—Br.

Three moles of bromine reacted with *m*-methoxybenzeneboronic acid to yield 2,4,5-tribromoanisole, G--Br, isolated in 57% yield.

Thus, groups with high capacities for conjugative electron release activate the *ortho* and *para* positions toward electrophilic attack to such an extent that the hydrogens in these positions are replaced preferentially. The fact that attack occurs in the position *para* to the methoxy group indicates that neither the steric effect nor the electron-withdraw-

⁽¹⁾ Preceding paper in this series: H. G. Kuivila and T. C. Muller, J. Am. Chem. Soc., 84, 377 (1962).

⁽⁴⁾ N. N. Melnikoff, J. Gen. Chem. U.S.S.R., 6, 636 (1936); Chem. Abstr., 30, 5571 (1936).

⁽⁸⁾ F. R. Bean and J. R. Johnson, J. Am. Chem. Soc., 54, 4415 (1932).

⁽¹⁰⁾ H. R. Snyder and C. Weaver, J. Am. Chem. Soc., 70, 232 (1948).

⁽¹¹⁾ H. G. Kuivila and A. R. Hendrickson, J. Am. Chem. Soc., 74, 5068 (1952).

ing effect of the boronic acid group plays any significant role in these reactions. Indeed, it may actually function as an *ortho* orienting group as it does in nitration in acetic anhydride. The steric effects of the boronic acid and methoxy groups must be substantial in F—Br. Here both groups are buttressed by adjacent bromine atoms, so that replacement of the boronic acid group, which does occur, might have been anticipated in this case.

Monochlorination of *m*-methoxybenzeneboronic acid with N-chloroacetamide and hydrogen chloride in aqueous solution gave unexpected results. The product proved to be a mixture of 2-chloro-5-methoxybenzeneboronic, B-Cl, and either 4chloro-3-methoxybenzeneboronic acid, C---Cl, or 2-chloro-3-methoxybenzeneboronic acid, D-Cl. They were characterized by hydrolysis to pand o-chloroanisole, respectively. On steric grounds it seems probable that the second isomer is the 4-chloro-3-methoxy compound. It is not obvious whether the difference in discrimination between bromination and chlorination is due to a specific orienting influence in bromination or simply a rather low degree of discrimination in attack by the more reactive chlorine, or both.

Each of the two chloroboronic anhydrides formed nicely crystalline 1:1 pyridine adducts. On the other hand, when a mixture of the isomers as obtained from the chlorination reaction was treated with diethanolamine, the crystalline product was identical in melting point and infrared spectrum with that obtained upon treatment of 2-chloro-5methoxybenzeneboronic acid, B-Cl with diethanolamine. Hydrolysis provided *p*-chloroanisole. Thus, the presence of the ortho-chloro substitutent appears to facilitate complex formation in this case. (The bromomethoxybenzeneboronic acids did not form diethanolamine complexes under the same conditions.) It might be argued that the orthosubstituent would interfere with co-planarity of the dihydroxyboron group with the ring necessary for maximum stabilization due to conjugation. In the absence of coplanarity formation of the quadricovalent complex might occur more easily. However, other work in this laboratory has indicated that intramolecular hydrogen bonding between the chlorine and the boronic hydroxyl group occurs to some extent. This would tend to stabilize the planar arrangement. A factor which might stabilize the complex would be hydrogen bonding between the N—H group of the complex and the ortho-chlorine as depicted in structure I-Cl. In the complex the nitrogen forms a coordinate bond to boron as suggested by the work of Musgrave and Park.¹² This in turn makes the hydrogen more acidic and increases its ability to participate in hydrogen bond formation to a degree greater than would normally be present in an aliphatic second-

CHART I

The specific halogen represented by X is indicated in the text by adding its symbol to the letter designating the structure in this chart-*i.e.*, B-Cl or D-Br



ary amine. Perhaps this factor is the decisive one in stabilizing the complex.



Direct iodination of *m*-methoxybenzeneboronic acid was not successful. However, reaction did occur with iodine chloride in carbon tetrachloride. It has been shown by Lambourne and Robertson,¹³ for example, that iodine monochloride can function as an iodinating or chlorinating agent if substitution must occur at a hindered position such as the 2- or 6- position in *p*-methylanisole. The extent of chlorination can be determined by the amount of iodine formed according to the equation

$$ArH + 2ICl \longrightarrow ArCl + HCl + I_2$$

In the present case it was found that two-thirds of the iodine chloride was used in iodination and the remainder in chlorination. The iodination product isolated was 2-iodo-5-methoxybenzene-

⁽¹²⁾ O. C. Musgrave and T. O. Park, Chem. & Ind., 1552 (1955).

⁽¹³⁾ L. J. Lambourne and P. W. Robertson, J. Chem. Soc., 1167 (1947).

The reaction between benzeneboronic acid and hypohalites. Reactions between benzeneboronic acids and halogens have usually been carried out in neutral or acidic solution.⁴ It has been shown that the rate of the reactions involving bromine and iodine increase with pH and proceed quantitatively.¹⁴ These facts suggested that benzeneboronic acids could be assayed quickly by reaction with excess halogen at high pH followed by determination of the amount of halogen consumed. Such a method of assay would be a useful supplement to the base titration in the presence of mannitol which is not entirely satisfactory for the weaker boronic acids. When bromine and benzeneboronic acid were allowed to react at pH > 12, the rate of reaction was very fast as expected, but more than one mole of bromine was consumed and the product was soluble in sodium hydroxide. Upon acidification of the reaction product a white solid precipitated. It was characterized by melting point and mixture melting point with an authentic sample as 2,4,6-tribromophenol.

Bromobenzene cannot be the primary product of the reaction as it is neither brominated nor hydroxylated by hypobromite. It seems most probable that the hydroxyl group replaced the boronic acid group first in an oxidation reaction and that the resulting phenol was then brominated, as in reactions 2 and 3.

$$\overbrace{}_{B}^{B}(OH)_{3}, Na^{+} + NaOBr + NaOH \rightarrow$$

$$\overbrace{}_{ONa}^{ONa} + NaBr + Na^{+}\overline{B}(OH)_{4}$$

$$\overbrace{}_{Br}^{Br}$$

$$\bigcirc$$
 ONa + 3NaOBr \longrightarrow Br \bigcirc ONa (3)
Br

Reaction (2) is rather slow compared with the succeeding steps. This was determined as follows. In reaction (2) all of the bromine in the hypobromite appears in the reaction product mixture as bromide ion; in reactions (3) none of this bromide appears as bromide. Thus a Volhard halide determination can be used to gain semiquantitative relative rate data. If reaction (2) were very much faster than reaction (3), essentially all of the first mole of hypobromite would be converted to bromide. If the reverse were true, one fourth of the first mole would be used in oxidation and the other three fourths in bromination of the phenol thus formed.

When equimolar amounts of hypobromite and benzeneboronic acid were allowed to react, 51%of the bromine was used in oxidation; a 20% yield (based on total boronic acid) of tribromophenol was isolated. When two moles of hypobromite per mole of boronic acid were used, 35% of the tribromophenol was obtained. An increase of the hypobromite-boronic acid molar ratio to four produced only 28% of tribromophenol. A second, tan product melting gradually above 180°, which could not be recrystallized, was obtained in substantial amount. Analysis revealed the approximate composition C₆H_{8.35}Br₂O. A similar product appeared when phenol was treated with four molar equivalents of hypobromite under comparable conditions. As it appeared thus to be a secondary product, it was not examined further.

With *p*-bromobenzeneboronic acid and three molar equivalents of hypobromite only tribromophenol was isolated (78% yield). This indicates that a *para* bromine increases the rate of reaction (2) to such an extent that hypobromite is never present in any significant excess over tribromophenol. Otherwise, some of the secondary product would be formed.

Hypochlorite gave results qualitatively similar to those obtained with hypobromite. Quantitative differences appeared, however. When four molar equivalents were used, it was necessary to heat the reaction mixture or to allow it to stand twelve hours in order to drive the reaction to completion. Up to 90% of 2,4,6-trichlorophenol, but no other product, was isolated. When only one molar equivalent of hypochlorite was used, 81% was used in oxidation and a mixture of phenol and o-chlorophenol was isolated.

When iodine was added to an alkaline solution of benzeneboronic acid, only 8% of the iodine was consumed in ten hours. The very small amount of oil which formed appeared to be iodobenzene.

The oxidation of the areneboronic acids to phenols by hypochlorite and hypobromite can be rationalized in terms of a mechanism entirely analogous to one involving the acids and hydrogen

$$\begin{array}{c} OH \\ ArB \rightarrow OH + Na \oplus, OX \xrightarrow{(a)} \\ Ar \rightarrow B \rightarrow OH \\ \end{array}$$

$$\begin{array}{c} OH \\ Ar \rightarrow B \rightarrow OH \\ O \rightarrow X \\ \hline OH \\ Ar \rightarrow B \rightarrow OH \\ \hline O + \\ \hline OH \\ Ar OH \\ + B(OH)_{3} \xrightarrow{(a)} Ar O \rightarrow B \rightarrow OH \end{array}$$

⁽¹⁴⁾ H. G. Kuivila and E. J. Soboczenski, J. Am. Chem. Soc., **76**, 2675 (1954); H. G. Kuivila and R. M. Williams, J. Am. Chem. Soc., **76**, 2679 (1954).

peroxide.¹⁵ In the present case, Equation 4, X is bromine or chlorine; in the peroxide case X is hydroxyl.¹⁶

EXPERIMENTAL

All melting points are uncorrected.

Monobromination of m-methoxybenzeneboronic acid. Two grams (0.0149 mole) of m-methoxybenzeneboronic anhydride were dissolved in 75 ml. of "20%" acetic acid.¹⁷ To this was added with stirring a solution of 2 g. of sodium bromide and 2.39 g. (0.0149 mole) of bromine in 25 ml. of "20%" acetic acid. Decolorization occurred immediately and white needles of product appeared. After standing in a refrigerator overnight, the product was filtered cold and air-dried. The yield was 2.60 g., 90%.

When attempts were made to crystallize this product from water, the solution became cloudy with *p*-bromoanisole formed by hydrolytic cleavage of the boronic acid group. The recovered product was less pure than that obtained from the reaction so the latter was used in the analysis.

Anal. Calcd. for C₇H₈O₈BBr: neut. equiv., 230.9; C, 36.43; H, 3.49; Br, 34.63. Found: neut. equiv., 231.5; C, 36.31; H, 3.60; Br, 34.38.

When placed in a melting point bath preheated to 117° , partial melting occurred within a minute. When the bath was preheated to 110° and the temperature raised at about $2^{\circ}/$ min. melting occurred only at $214-216^{\circ}$.

A sample of the above acid was dried at 95° for 1 hour yielding the anhydride, m.p. 213-215° unchanged upon crystallization of 2.5 g. from 100 ml. of water, followed by ovendrying as before. Upon standing for several months a sample of this anhydride reverted partially to the acid, a behavior unusual for areneboronic acids.

Anal. Calcd. for $C_7H_6O_2BBr$: neut. equiv., 212.9; C, 39.54; H, 2.85. Found: neut. equiv., 211.2; C, 39.31; H, 2.70.

Hydrolysis of 2-bromo-5-methoxybenzeneboronic acid, B-Br. —Two grams (0.0147 mole) of zinc chloride, 2.15 g. (0.0093 mole) of 2-bromo-5-methoxybenzeneboronic acid and 10 ml. of water were placed in the pot of a micro liquid-liquid extractor fitted with a chamber¹⁸ for extraction of water solutions with solvents of lower density. Upon heating the pot an oil separated. When the solution was refluxed the oil was steam-distilled and accumulated in the extraction chamber. After 0.5 hr. of reflux the condensate no longer separated into two phases. The oil was removed with a capillarytipped pipe; 1.1 ml. or 1.61 g. (92%) of p-bromoanisole, n^{25} D 1.5588, was obtained. Its sulfonamide derivative¹⁹ was prepared and had m.p. 150.5-151.3° (lit.¹⁹ 147-148°) undepressed upon admixture with sulfonamide prepared from authentic p-bromoanisole.

Dibromination of m-methoxybenzeneboronic acid. The procedure was similar to that used for the monobromination except that twice as much each of bromine and sodium bromide were used. The reaction was somewhat slower so the reaction mixture was allowed to stand two days before filtration; yield of air-dried product: 4.15 g. (92%). When the neutral equivalent was determined, the reaction of the mannitol-boronic acid solution with sodium hydroxide was rather slow during the last half of the titration, requiring about 1 hr. before a permanent end-point was reached. This endpoint was reproducible within the usual limits of less

(16) As suggested by a referee, steps (b) and (c) might occur together; this would probably be a more favorable path energetically.

(17) Made from 1 vol. of glacial acetic acid and 4 vol. of water.

(18) Scientific Glass Apparatus Co., Bloomfield, N. J., Cat. No. MO-390.

(19) E. R. Huntress and F. H. Carter, J. Am. Chem. Soc., 62, 511 (1940).

than $\pm 0.5\%$. Inasmuch as the melting behavior was similar to that of the monobromo acid no meaningful melting point could be determined. As shown by the analysis below, the product was a monohydrate of 2,4-dibromo-5-methoxyben-zeneboronic acid, F—Br.

Anal. Calcd. for C₇H₉O₄BBr₂: neut. equiv., 327.8; C, 25.66; H, 2.77; Br, 48.76. Found: neut. equiv., 327.0; C, 25.48; H, 2.80; Br, 48.64.

Reaction of the dibromomethoxybenzeneboronic acid. F-Brwith hydrogen peroxide. To 2.0 g. (9.68 mmoles) of the dibromomethoxybenzeneboronic acid in 5 ml. of methanol was added 2.5 ml. of 3.87*M* hydrogen peroxide (9.68 mmoles). The reaction mixture became warm. After standing for 24 hr., the methanol was evaporated on a steam bath and the resulting oil extracted with petroleum ether. Evaporation of the latter yielded 2.07 g. (76%) of a yellow oil with a phenolic odor. Repeated recrystallization from petroleum ether accompanied by treatment with Norite ultimately yielded 0.52 g. (19%) of pure 2,4-dibromo-5-methoxyphenol H-Br; m.p. 68-69°, undepressed upon admixture with material of m.p. 67-68° prepared by the method of Kohn.²⁰

Tribromination of m-methoxybenzeneboronic acid. As the reaction of m-methoxybenzeneboronic acid with 3 moles of bromine was quite slow, sodium acetate was used as a catalyst. One gram (7.47 mmoles) of the boronic acid anhydride and 2.5 g. (30.8 mmoles) of sodium acetate were dissolved in a solution of 20 ml. of methanol and 40 ml. of water. A vial containing 3.58 g. (22.4 mmoles) of bromine was introduced and the mixture shaken until the bromine dissolved. The solution became cloudy, an orange oil separated and solidified, and more precipitate formed. In a few minutes the solution was yellow and after 5 days it was colorless. (In the absence of sodium acetate the reaction was incomplete even after 8 days.) The resulting solution was evaporated on a steam bath until a semisolid residue remained. This was triturated with hot benzene and the resulting benzene solutions evaporated near dryness and extracted with 10% sodium hydroxide leaving 1.46 g. (57%) of a white solid. After recrystallization twice from ethanol 0.80 g. of 2,4,5-tribromoanisole, G-Br, was obtained; m.p. 105-106° undepressed upon admixture with an authentic sample of m.p. 105-105.5° prepared by dibromination²¹ and methylation from *m*-bromophenol.

Chlorination of m-methoxybenzeneboronic acid. To 2.0 g. of m-methoxybenzeneboronic acid dissolved in the minimum amount of hot water was added 1.41 g. of N-chloroacetamide followed by 5 ml. of concd. hydrochloric acid. The mixture was allowed to cool to room temperature. Filtration provided 1.2 g. (43%) of a chloromethoxybenzeneboronic acid, m.p. 115°, resolidifying and remelting at 190-195°. Recrystallization gave the anhydride of 2-chloro-5-methoxybenzene boronic acid, B—Cl, with variable melting point, the highest observed being 220-223°.

Anal. Calcd. for $C_7H_8O_2BCl$: C, 45.11; H, 4.32; Cl, 19.02. Found: C, 44.83; H, 4.60; Cl, 19.20.

Cooling of the filtrate yielded another 1.2 g. (43%) of crystals of the isomeric 4-chloro-3-methoxybenzeneboronic acid, C—Cl, m.p. 146-151°.

Anal. Calcd. for C₇H₈O₂BCl: C, 45.11; H, 4.32; Cl, 19.02. Found: C, 44.98; H, 4.20; Cl, 18.96.

Pyridine complexes of the chloromethoxybenzeneboronic anhydrides. Three milliliters of a pyridine-ether solution containing 0.047 g. of pyridine was added to 0.3 g. of compound B—Cl. The anhydride dissolved and crystals appeared immediately; m.p. 172–175°.

Anal. Calcd. for C₂₅H₂₃O₆Cl₃B₂N: C, 53.46; H, 3.97; N, 2.41, Cl, 18.22. Found: C, 53.64; H, 4.20; N, 2.60; Cl, 18.38. In a similar way the pyridine complex of C-Cl was ob-

In a similar way the pyridine complex of C—Cl was obtained by reaction of 0.30 g. with 0.053 g. of pyridine; m.p. $156-159^{\circ}$.

⁽¹⁵⁾ H. G. Kuivila, J. Am. Chem. Soc., 76, 870 (1954).

⁽²⁰⁾ M. Kohn, J. Am. Chem. Soc., 74, 1601 (1952).

⁽²¹⁾ H. H. Hodgson, J. Walker, and J. Nixon, J. Chem. Soc. 1053 (1933).

Anal. Calcd. for $C_{26}H_{23}O_6B_3Cl_3N$: C, 53.46; H, 3.97; N, 2.41; Cl, 18.22. Found: C, 53.46; H, 4.17; N, 2.56; Cl, 18.41.

Hydrolysis of B-Cl and C-Cl. Two grams of the boronic anhydride and 2 g. of zinc chloride were dissolved in 15 ml. of water and refluxed in the semimicro liquid-liquid extractor for 19 hr. The chloroanisoles were separated from the liquid in the upper chamber, dried over potassium hydroxide, and their infrared spectra taken and found to be identical with those of authentic samples of o- and p-chloroanisole, respectively.

Reaction of B--Cl and C--Cl with diethanolamine. To 1 g. of a mixture of the two boronic acids was added 2 g. of diethanolamine. A crystalline solid, m.p. $187-189^{\circ}$ soon appeared. Its infrared spectrum contained an N-H stretching band at 3140 cm.⁻¹, characteristic of the diethanolamine complexes.¹² Without further characterization the product was hydrolyzed, first with dilute hydrochloric acid to the boronic acid, and the latter with aqueous zinc chloride to *p*chloroanisole showing none of the bands characteristic of the *ortho* isomer.

Iodination of m-methoxybenzeneboronic acid. To a solution of 2 g. of m-methoxybenzeneboronic anhydride in 70 ml. of carbon tetrachloride was added 2.8 g. of iodine chloride in 20 ml. of the same solvent. The mixture was warmed on the steam bath for 15 min. and then cooled in a refrigerator. The crystals which precipitated were removed, and the iodine-containing filtrate titrated with thiosulfate, indicating the presence of 4.24 mmoles of iodine as compared with 17.0 mmoles of iodine chloride originally present. Thus, just onequarter of the iodine chloride was used in chlorination, and one-half in iodination. The 2.3 g. (65%) of 2-iodo-5-methoxybenzeneboronic acid which had been removed was recrystallized several times from carbon tetrachloride providing ultimately 0.77 g. of the anhydride; m.p. 84-87°. The neutralization equivalent, determined potentiometrically, was found to be 260 vs. the theoretical 259.8. The resulting solution contained crystals of p-iodoanisole m.p. 51-53°, undepressed on admixture with an authentic sample. The anhydride reverted readily to the acid which was analyzed.

Anal. Calcd. for $C_7H_8O_8BI$: C, 30.5; H, 2.88; I, 45.4. Found: C, 30.56; H, 2.89; I, 44.13.

The filtrate from the first filtration was worked up, and yielded 0.38 g. of crude chloromethoxybenzeneboronic anhydrides, m.p. 91-94°.

Reaction between equimolar amounts of hypobromite and benzene-boronic acid. To 50 ml. of water were added 4.0 g. (100 mmoles) of sodium hydroxide and 0.80 g. (10 mmoles) of bromine and 1.04 g. (10 mmoles) of benzeneboronic anhydride. After 15 min. the bromine was all consumed. Determination of bromide on an aliquot showed that 4.9 mmoles of bromine had been used in substitution and 5.1 mmoles used in oxidation (replacement of the boronic acid group by hydroxyl). Acidification and filtration of the main bulk of the reaction mixture yielded 20% (based on initial boronic acid) of 2,4,6-tribromophenol; m.p. 79.5-82.5°.

Reaction between hypobromite and benzeneboronic acid in 4:1 ratio. A solution of 19.5 mmoles of sodium hypobromite in 50 ml. of water was added to a solution of 0.59 g. (4.88 mmoles) of benzeneboronic acid in 20 ml. of water. After one hour the product was acidified with dilute nitric acid and filtered. The precipitate was dried in the air yielding 1.3 g. of which 0.8 g. was insoluble upon treatment with 5 ml. of ethanol. This material was analyzed. Found: C, 28.16%; H, 1.32%, Br, 64.52%. Using the benzene ring as a basic unit this corresponds to an empirical formula $C_6H_{3.45}Br_2O$.

Addition of water to the ethanol filtrate yielded 0.42 g. (28% yield) of 2,4,6-tribromophenol, m.p. 90-91°.

Reaction between hypobromite and p-bromobenzeneboronic acid. A solution of 15 mmoles of bromine and 28 mmoles of sodium hydroxide in 10 ml. of water was added to 5 mmoles of p-bromobenzeneboronic acid and 15 mmoles of sodium hydroxide in 10 ml. of water. After an hour the reaction product was acidified and the tribromophenol filtered and dried: 1.29 g., 78% yield, m.p. 92°.

The tribromophenol samples obtained in the experiments described gave no melting point depression when mixed with the authentic compound, m.p. 95–96°.

Reactions between hypochlorite and benzeneboronic acid. To a solution of 9.63 mmoles of benzeneboronic acid in 5 ml. of water was added a solution of 40.45 mmoles of sodium hypochlorite in 75 ml. of water. The solution was heated to 80° for one hour, cooled, treated with 1 g. of sodium bisulfite, acidified, and filtered. The crude trichlorophenol was steam distilled yielding 90% of 2,4,6-trichlorophenol, m.p. 67.5-68°, undepressed when mixed with an authentic sample.

The *p*-nitrobenzoate ester was prepared²² and found to have m.p. $103.5-105^{\circ}$, undepressed on admixture with the ester made from the authentic sample of the phenol.

When the above experiment was carried out with equimolar quantities of hypochlorite and benzeneboronic acid a liquid phenol mixture was obtained. Distillation yielded a main fraction (80% of the product) b.p. $182-187^\circ$, whose *p*nitrobenzoate corresponded to that of phenol. Of the benzeneboronic acid used 15% was recovered.

Further evidence that the oxidation reaction is faster than the chlorination of the phenol is the following. A solution of 10 mmoles of sodium hypochlorite and 10 mmoles of benzeneboronic acid in 25 ml. of water was heated at 80° for 0.5 hr. Chloride analysis showed that 8.11 mmoles of the hypochlorite had been used for oxidation and 1.89 mmoles had been involved in nuclear chlorination.

DURHAM, N. H.

(22) A. I. Vogel, A Textbook of Practical Organic Chemistry, Longmans, Green & Co., New York, 1948, p. 656.