(although the $N(CH_3)_3^+$ group generally does fit). It is likely, therefore, that charged substituents involve additional complications. The nature of the inductive effects of charged substituents will be considered further in later publications.

TABLE III

VALUES OF ρ_I FOR ACID IONIZATIONS IN WATER, 25°

	Acid	ρ_I
1.	$C_6H_5NH_3^+$	2.83
2.	C_6H_5SH	2.93
3.	C_6H_5OH	2.30
4.	$C_6H_5B(OH)_2$	2.15
5.	C_6H_5COOH	1.00
6.	$C_6H_5P(OH)_2$ (O)	0.76
7.	$C_6H_5P(OH)$—OH (O)	0.95
8.	$C_6H_5As(OH)_2$ (O)	1.05
9.	$C_6H_5As(O^-)$—OH (O)	0.87
10.	C_6H_5Se—OH (O)	0.91
11.	$C_6H_5CH_2NH_3^+$	0.72
12.	$C_6H_5CH_2COOH$	+0.49
13.	$C_6H_5CH_2CH_2COOH$	+0.21

Table III lists ρ_I values obtained for a number of acid ionization equilibria in aqueous solution. The values given for acids 6–13 are actually the Hammett ρ values given by Jaffé, since too few data are available in most of these reaction series to apply equation 7. The ρ_I and ρ values for these acids are expected to be quite similar, although when comparison is possible the relationship discussed in the following paragraph is frequently followed more closely by ρ_I values.

The important point illustrated in Table III is that to a rough approximation ρ_I depends only upon the position with respect to the benzene ring at which ionization occurs in the side-chain. Acid ionizations (1–3) in which the formal charge on the first atom of the side-chain is decreased by one unit have ρ_I values of 2.3 to 2.9. If the unit decrease in formal charge acts through an additional atom, ρ_I values of 0.72 to 1.05 are obtained (acids 5–11). Acids 12 and 13 provide further examples of the applicability of the equation: $\rho_I \cong (2.8 \pm 0.5)^{1-i}$, where i = the number of saturated atoms between the benzene ring and the atom at which the unit decrease in formal charge takes place. This relationship is followed in a manner roughly independent of the charge type of the acid or the kind of atom involved, and conforms to the Branch and Calvin scheme for treating inductive effects in acid ionization equilibria.[24]

The ρ_I value of phenylboric acid (4) is of special interest. Although the proton leaves from the second atom of the $-B\langle^{OH}_{OH}$ group, the conjugate base is probably adequately represented by the major resonance form, $(C_6H_5\text{-}B^{-1}\langle^{O}_{OH})^-$, so that the *first* atom loses nearly a unit formal charge on ionization of the acid. Accordingly, the ρ_I value is nearer to that for acids 1–3 than 5–11.

Having used equation 7 to demonstrate the general applicability of the σ_I inductive scale, and to determine the inductive reaction constant, ρ_I, we are now in a position to evaluate the total resonance effect by applying equation 1 in the form

$$\text{total effect of reson.} \equiv \log (k^p/k_0) - \sigma_I\rho_I \text{ for } p\text{-substituent}$$
$$\text{total effect of reson.} \equiv \log (k^m/k_0) - \sigma_I\rho_I \text{ for } m\text{-substituent} \quad (9)$$

Equation 9 can be used to examine the general applicability and limitations of the σ_R resonance scale, and to establish the nature of the dependence of resonance effects on reaction type. The next paper in this series will deal with such an examination.

Acknowledgment.—The authors wish to express their appreciation to Professor H. H. Jaffé for the benefit of valuable discussions.

(24) Reference 6b, pp. 193–200. NOTE ADDED IN PROOF.—The ionization of pyridinium ions in H_2O, 25°, with $\rho = +5.69$, (H. H. Jaffé and G. O. Doak, THIS JOURNAL, **77**, 4441 (1956)) also conforms to this rough scheme. The formal charge of the nitrogen atom of the ring is decreased by one in the ionization, corresponding in the above formulation to $i = -1$.

UNIVERSITY PARK, PENNA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF UTAH]

Cyclic Benzeneboronate Esters

BY JAMES M. SUGIHARA AND CARLOS M. BOWMAN

RECEIVED NOVEMBER 18, 1957

Reaction products of benzeneboronic acid with *cis*- and *trans*-cyclopentane-1,2-diol, *cis*- and *trans*-cyclohexane-1,2-diol, pyrogallol, methyl β-D-glucopyranoside, 2,3-butanediol, 1,3-butanediol, 1,4-butanediol, 3,4-di-*O*-benzoyl-D-mannitol and galactitol are described in addition to the previously prepared tribenzeneboronates of D-mannitol and D-glucitol. Ring structures containing 5-, 6- or 7-members are possible. Polyols tend to form completely substituted benzeneboronates. An explanation, based upon ease of hydrolysis and method of preparation, is offered for the latter observation.

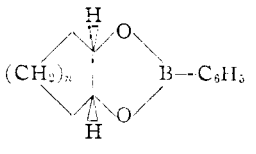
Cyclic boronate esters of the compounds D-mannitol, D-glucitol, pinacol, pentaerythritol, diethyl D-tartrate, *cis*-indane-1,2-diol and catechol are reported.[1] Reaction was effected in aqueous media in all cases. Benzeneboronate esters of pentoses and two 6-deoxyhexoses were prepared[2] by fusing the two reagents. However, knowledge concerning steric requirements for ring formation and preferred ring size is largely lacking. Accordingly, this investigation was initiated in the hope of obtaining some information in this direction.

Cyclic diols were selected as model compounds to study the possibility of formation of cyclic boronate esters, since the relative positions of the hydroxyl groups are essentially fixed. Refluxing of

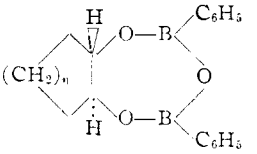
(1) H. G. Kuivila, A. H. Keough and E. J. Soboczenski, *J. Org. Chem.*, **19**, 780 (1954).

(2) M. L. Wolfrom and J. Solms, *ibid.*, **21**, 815 (1956).

benzeneboronic acid with *cis*-cyclopentane-1,2-diol and with *cis*-cyclohexane-1,2-diol in anhydrous acetone followed by distillation (procedure A) gave crystalline benzeneboronates (I, II) of low melting points. Since the esters of the *trans*-isomers were



I, $n = 1$
II, $n = 2$



III, $n = 1$
IV, $n = 2$

crystalline compounds with higher melting points, they were purified by recrystallization (procedure B). On the basis of elemental analyses and molecular weight determinations, the ester of *trans*-cyclopentane-1,2-diol has been assigned structure III and the ester of the cyclohexane homolog, structure IV.

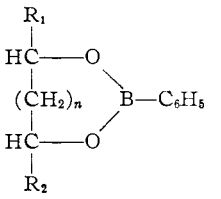
The difference in behavior of the cyclopentanediol isomers is interpretable by the knowledge that the carbon–oxygen bonds in the *cis* isomer are essentially coplanar while those in the *trans* isomer are distinctly not. The proposed seven-membered ring structure is possible, as demonstrated by a molecular model.

The variance in reactivity of the two cyclohexanediols has been reviewed.[3] The energy requirements for *cis* functions to move into a coplanar position are small, since the movement involved resembles the partial inversion of a chair form into a boat form. The forcing of two *trans* groups into essentially coplanar positions reduces the distance between axial atoms and increases strain in the ring. Assuming that benzeneboronate ester formation requires a coplanar intermediate, the difference in type of products formed from *cis*- and *trans*-cyclohexane-1,2-diol is understandable.

Another polyhydroxyl compound, which appeared to be of interest, was pyrogallol, since all of its oxygen atoms are coplanar with the ring. A pyrogallol monobenzeneboronate readily was obtained. Benzoylation of this compound yielded the monobenzoate. Hydrolysis of the benzeneboronate ester group was then effected by the addition of D-mannitol to an aqueous solution of the compound and neutralizing the complex formed. The pyrogallol benzoate obtained is apparently the same as the compound previously reported,[4] and is probably the 1-benzoate, since the compound is readily oxidizable. The attempted methylation of the monobenzoate with diazomethane failed. Acetylation of pyrogallol benzeneboronate gave pyrogallol triacetate. Apparently the ester linkage is not stable toward acetylation conditions.

Since methyl β-D-glucopyranoside had been found to be a useful substrate in studying the reaction of boric acid with polyols,[5] the compound was applied in this investigation. The reaction of two moles of benzeneboronic acid per mole of the glucoside yielded an amorphous product, whose character was studied by the previously described procedure[5] of benzoylation, hydrolysis and acetylation. The only isolable product was methyl β-D-glucoside tetraacetate (71%), indicating essentially complete blocking of all the hydroxyl groups. Application of the same procedure to an equimolar mixture of the reactants gave a reaction mixture, separable by chromatography, containing methyl β-D-glucoside tetrabenzoate (37%) and the tetraacetate (41%). These observations indicate that nearly one-half of the glucoside reacted completely at the site of all of the hydroxyl groups with benzeneboronic acid, and a substantial amount of the remainder of the reagent did not react. Since the chromatographic procedure has been demonstrated[5] to separate any diacetate dibenzoates, it is likely that the total amount of monobenzeneboronate esters in the reaction mixture is small.

Alkanediols were allowed to react with benzeneboronic acid to determine any preference for ring size. 2,3-Butanediol, 1,3-butanediol and 1,4-butanediol formed distillable products in yields of 81, 88 and 71%, respectively, and assigned structures V, VI and VII, respectively. Under the same



V, $R_1 = R_2 = CH_3$; $n = 0$
VI, $R_1 = H$; $R_2 = CH_3$; $n = 1$
VII, $R_1 = R_2 = H$; $n = 2$

experimental conditions, 1,5-pentanediol gave no distillable or crystallizable product. Thus formation of five-, six- and seven-membered rings was indicated but not an eight-membered ring. From percentage yields the five- and six-membered ring compounds appear to form somewhat more readily than the seven-membered ring.

The tribenzeneboronate ester of D-mannitol has been previously described.[1] However, the size of the boronate ring system has not been established. In order to obtain information which might provide a more precise structural assignment, the hexitol was treated with benzeneboronic acid in various molar ratios. Reaction was effected in anhydrous acetone. Petroleum ether extractions of the solids derived provided high yields (94% with three moles of benzeneboronic acid) of the crystalline product (procedure C). When this procedure was followed using two moles of benzeneboronic acid per mole of D-mannitol, the crystalline triboronate was isolated in an amount accounting for 92% of the benzeneboronic acid. When the amorphous reaction mixture was benzoylated, followed by hydrolysis of boronate ester groups, D-mannitol hexabenzoate was the only isolable crystalline compound, accounting for 25% of the original hexitol. If the triboronate ester formation should consume all of the benzeneboronic acid, one-third of the mannitol should remain unreacted and therefore yield the hexabenzoate.

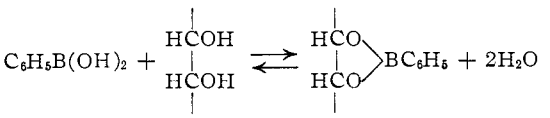
In the above procedure C, solubilities of reactants and product in acetone might tend to favor the formation of the triboronate ester, since D-mannitol has low solubility in this solvent and benzeneboronic acid is highly soluble. A modification

(3) D. H. R. Barton and R. C. Cookston, *Quart. Rev.*, **10**, 81 (1956).
(4) A. Einhorn and F. Hollandt, *Ann.*, **301**, 95 (1898).
(5) J. M. Sugihara and J. C. Petersen, THIS JOURNAL, **78**, 1760 (1956).

of this procedure was applied to maintain an excess of D-mannitol in the reaction mixture (procedure D). An acetone–water solution of benzeneboronic acid was added to an aqueous acetone solution of D-mannitol. Petroleum ether extraction of the reaction residue yielded only the triboronate ester. Application of procedures C and D with D-glucitol and galactitol gave the tribenzeneboronate esters only in high yields.

The ease of hydrolytic cleavage of benzeneboronate esters of several sugars is reported.[2] A study of the ease of hydrolysis of D-mannitol tribenzeneboronate appeared desirable, since the compound is preparable in an aqueous medium.[1] The hydrolysis of 0.5 g. of the ester in 50 ml. of water was incomplete, as shown by the incomplete recovery of benzeneboronic acid. A 10% hydrochloric acid solution effects a greater degree of hydrolysis. Optical rotation data indicated that the ester is stable in anhydrous solvents but readily hydrolyzed in moist acetone or pyridine.

These observations obtained using D-mannitol may be rationalized by assuming that a readily-reversible equilibrium reaction is involved.



In any system containing water, the point of equilibrium lies considerably to the left. However, water insolubility of the triboronate ester of D-mannitol permits its formation even in an aqueous medium.[1] In procedure D, little reaction might be expected because of the water present. Removal of acetone would bring about ester formation and its precipitation as a result of its water insolubility. The mono- and disubstituted derivatives of D-mannitol would be expected to have greater water solubility and would not, therefore, be isolable.

An additional compound, D-mannitol 3,4-dibenzoate, previously undescribed, was allowed to react with benzeneboronic acid. A crystalline diboronate ester was obtained, and assigned the structure D-mannitol 3,4-dibenzoate 1,2:5,6-dibenzeneboronate.

Reaction products of 2-aminoethanol and *o*-aminophenol with benzeneboronic acid were obtained but were found to be unstable. Bromination and acylation of *o*-aminophenol benzeneboronate failed to yield expected products.

One (C.M.B.) of us gratefully acknowledges support from a University Research Committee Fellowship.

Experimental[6]

Benzeneboronic acid,[7] m.p. 215–217°, ***trans*-1,2-cyclohexanediol,**[8] m.p. 102–103°, ***cis*-1,2-cyclohexanediol,**[9] m.p. 98–99°, ***trans*-1,2-cyclopentanediol,**[8] m.p. 50°, and ***cis*-1,2-cyclohexanediol,**[9] b.p. 105–110° (15 mm.), were prepared by methods described in the literature.

3,4-Di-*O*-benzoyl-D-mannitol.—A solution containing 20 g. of 1,2:5,6-di-*O*-isopropylidene-D-mannitol[10] in 100 ml. of anhydrous pyridine was cooled to 0° and 12.5 ml. of benzoyl chloride was added while agitating. The resulting suspension was allowed to stand at room temperature for 15 hr. and then poured over ice and water. The mixture was vigorously stirred for 0.5 hr. and then extracted with 300 ml. of ether. The ether extract was washed twice each with 50-ml. portions of 2 *N* hydrochloric and 2 *N* sodium hydroxide, and once with 75 ml. of water. The ether solution was dried over anhydrous sodium sulfate. Evaporation of solvent under reduced pressure left a sirup (37.7 g.), which failed to crystallize. A solution of 8.0 g. of the sirup, 20 ml. of acetone, 0.5 ml. of 12 *N* hydrochloric acid and 2 ml. of water was refluxed for 5 hr. Barium carbonate (5 g.) was added to neutralize the acid. The solids were removed by filtration. The filtrate was evaporated on a steam-bath under reduced pressure, leaving a white amorphous solid, which was crystallized from absolute ethanol. Recrystallization from ethanol gave 2.8 g. (44%) of 3,4-di-*O*-benzoyl-D-mannitol, m.p. 183–185°, $[\alpha]^{28}D$ +1.12° (*c* 4.02, pyridine).

Anal. Calcd. for $C_{20}H_{22}O_8$: C, 61.53; H, 5.68. Found: C, 61.41; H, 5.49.

Benzeneboronic Esters of Alcohols, Phenols and Amines.—Four general procedures are described for the preparation of compounds listed in Table I.

Procedure A.—A solution of 0.043 mole of a diol (aminoalcohol, aminophenol or diamine), 0.043 mole of benzeneboronic acid and 20 ml. of anhydrous acetone was refluxed for 4 hr. The acetone was removed under reduced pressure on a steam-bath. The remaining clear viscous liquid was transferred to a Claisen flask and distilled under reduced pressure.

Procedure B.—The same reaction mixture, as described in procedure A, was refluxed for 4 hr. Upon cooling the acetone solution, crystallization occurred. Recrystallization from acetone yielded purified samples.

Procedure C.—A solution of 0.0055 mole of a polyol (or phenol), 0.011 (0.0055 or 0.0165) mole of benzeneboronic acid and 20 ml. of anhydrous acetone was refluxed for 4 hr. in an anhydrous system. Removal of the acetone under reduced pressure over a steam-bath left a white amorphous solid. Extraction of the boronate ester was effected by refluxing this residue with three 75-ml. portions of petroleum ether (b.p. 110–125°) for 25 min. each time. When the combined petroleum ether extracts were cooled, crystallization occurred. Purification was effected by recrystallization from petroleum ether.

Procedure D.—A solution of 0.0055 mole of a polyol in 20 ml. of acetone and 10 ml. of water was heated to the reflux temperature over a steam-bath. A solution containing 0.0055 (or 0.011) mole of benzeneboronic acid, 20 ml. of acetone and 10 ml. of water was added slowly to the reaction mixture over a period of 0.5 hr. After this addition was completed, the solution was refluxed for 4 hr. longer. Removal of acetone under reduced pressure over a steam-bath left a white amorphous solid, which was treated in the same manner as described in procedure C.

Tribenzeneboronates of hexitols were obtained by either procedure C or D, when molar ratios of hexitols to benzeneboronic acid of one to one, one to two, and one to three were applied; the following data were obtained: (hexitol, yield, melting point) D-mannitol 75–94%, 135° (reported[1] 66%, 133–135°); D-glucitol, 81–98%, 194° (reported[1] 66%, 187–189°); and galactitol, 90%, 162–163°.

Anal. Calcd. for $C_{24}H_{23}O_6B_3$: C, 65.53; H, 5.27; B, 7.38. Found: C, 65.09; H, 5.27; B, 7.29.

Benzoylation of Pyrogallol Benzeneboronate.—A solution of 2 g. of pyrogallol benzeneboronate and 10 ml. of anhydrous pyridine was cooled to 5° and a solution of 4.0 g. of benzoyl chloride and 10 ml. of anhydrous pyridine was added slowly while agitating. The resulting suspension was allowed to stand for 8 hr. at room temperature. Absolute ethanol (30 ml.) was added in portions, and the resulting solution was allowed to stand for an additional hour. All the solvents were evaporated by passing a jet of air over the solution to leave a white, crystalline residue. Recrystalli-

(6) All melting points are corrected. C and H analyses were made by Drs. G. Weiler and F. F. Straus, Oxford, England. Boron was determined by hydrolysis of esters and titration of the released benzeneboronic acid (G. E. K. Branch, D. L. Yabroff and B. Bettman, THIS JOURNAL, **56**, 937 (1934)). Molecular weights were determined cryoscopically in benzene.

(7) F. R. Bean and J. R. Johnson, THIS JOURNAL, **54**, 4415 (1932).

(8) A. Roebuck and H. Adkins, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 217.

(9) N. A. Milas and S. Sussman, THIS JOURNAL, **59**, 2345 (1937).

(10) E. Baer and H. O. L. Fischer, *J. Biol. Chem.*, **128**, 463 (1939).

TABLE I

BENZENEBORONATES OF ALCOHOLS, PHENOLS AND AMINES

Reagent	B.p. °C.	Mm.	M.p., °C.	Formula	Analyses, % Calculated C	H	B	Found C	H	B	Procedure	Yield, %
cis-1,2-Cyclohexanediol	95	0.3	42–43	$C_{12}H_{15}O_2B$	71.32	7.48	5.35	71.84	7.28	5.32	A	97
trans-1,2-Cyclohexanediol			134–136	$C_{18}H_{20}O_3B_2$[a]	70.65	6.59	7.07	70.82	6.64	6.91	B	60
cis-1,2-Cyclopentanediol	80–82	1	15–17	$C_{11}H_{13}O_2B$	70.26	6.97	5.75	70.03	7.03	5.64	A	95
trans-1,2-Cyclopentanediol			127–128	$C_{17}H_{18}O_3B_2$[b]	69.69	6.19	7.39	70.14	6.38	7.24	B	74
Pyrogallol			166	$C_{12}H_9O_3B$[c]	67.98	4.28	5.10	68.04	4.38	4.92	C	90
2,3-Butanediol	75–77	1		$C_{10}H_{13}O_2B$	68.23	7.44	6.15	68.44	7.51	6.05	A	81
1,3-Butanediol	85–86	1		$C_{10}H_{13}O_2B$	68.23	7.44	6.15	68.69	7.52	5.99	A	88
1,4-Butanediol	90–95	1		$C_{10}H_{13}O_2B$	68.23	7.44	6.15	68.55	7.60	6.03	A	71
1,5-Butanediol	>300	1									A	0
3,4-Di-*O*-benzoyl-D-mannitol			149–150	$C_{22}H_{28}O_8B_2$[d]	68.38	5.02	3.85	67.99	5.08	3.82	C[e]	84
2-Aminoethanol	80–85	2[f]			(Decomposes)						A	21
o-Aminophenol	140–145	2[f]	99–101		(Decomposes)						A	81
o-Phenylenediamine					(Decomposes upon distillation)							

[a] Molecular weight: calcd. 306; found 310. [b] Molecular weight: calcd. 292; found 297. [c] Gives a green-colored solution in alcoholic ferric chloride. [d] $[\alpha]^{28}D$ +2.35° (*c* 2.52, pyridine). [e] Crystallized and recrystallized from ethanol. [f] Distillation in nitrogen atmosphere.

zation from absolute ethanol gave 1.9 g. (65%) of pyrogallol benzeneboronate benzoate, m.p. 169–170°.

Anal. Calcd. for $C_{19}H_{13}O_4B$: C, 72.18; H, 4.14; B, 3.42. Found: C, 72.43; H, 4.18; B, 3.36.

Pyrogallol Benzoate.—Pyrogallol benzeneboronate benzoate (4.0 g.) was dissolved in 25% ethanol. D-Mannitol (4.0 g.) was added to this solution, and 2.0 g. of sodium bicarbonate was introduced in portions to the resulting mixture to neutralize the mannitol–benzeneboronate complex. The resulting solution was extracted three times with 50-ml. portions of ether. The combined ether solution was dried over anhydrous sodium sulfate and then evaporated to a sirup, which crystallized upon adding a small volume of chloroform, giving 2.1 g. (72%) of pyrogallol benzoate, m.p. 138–139°. Two recrystallizations from chloroform raised the melting point to 141°, reported[4] 140°.

The attempted methylation of pyrogallol benzoate with diazomethane yielded only the starting phenol. Pyrogallol benzoate reacted readily with Tollens reagent.

Acetylation of Pyrogallol Benzeneboronate.—A solution of 3.15 g. of pyrogallol benzeneboronate, 30 ml. of anhydrous pyridine and 15 ml. of acetic anhydride was allowed to stand overnight. Absolute ethanol (75 ml.) was added to the solution, and the resulting solution was allowed to stand for an additional hour. Evaporation of the solvents by passing a jet of air over the solution left a sirup. The latter was dissolved in a minimum volume of absolute ethanol. Crystallization from ethanol yielded 3.47 g. (93%) of pyrogallol triacetate, m.p. 164–165° (reported[11] 165°).

Anal. Calcd. for $C_{12}H_{12}O_6$: C, 57.14; H, 4.79. Found: C, 57.12; H, 4.65.

Methyl β-D-Glucopyranoside Benzeneboronate.—When two moles of benzeneboronic acid per mole of methyl β-D-glucopyranoside was treated as given in procedure C, an amorphous solid was obtained. This was processed by the general technique applied to borate esters[5] of benzoylation, hydrolysis and acetylation. Five grams of the glucoside yielded 6.7 g. (71%) of methyl β-D-glucoside tetraacetate, m.p. 103–105°, alone or admixed with an authentic sample.

The same series of reactions using equimolar amounts of methyl β-D-glucopyranoside (0.5 g.) and benzeneboronic acid gave a sirup. Chromatographic separation[5] gave 0.37 g. (41%) of methyl β-D-glucopyranoside tetraacetate, m.p. 103–105°, alone or admixed with an authentic sample, and 0.59 g. (37%) of methyl β-D-glucopyranoside tetrabenzoate, m.p. 160–162°, alone or admixed with an authentic sample.

D-Mannitol Benzeneboronate.—The amorphous solid obtained by the reaction of two moles of benzeneboronic acid per mole of D-mannitol (1.0 g.) was benzoylated in the usual manner. Chromatography of the resulting sirup gave 0.19 g. (25%) of D-mannitol hexabenzoate, m.p. 149–150°, alone or admixed with an authentic sample.

Hydrolysis of D-Mannitol Tribenzeneboronate.—A suspension of 0.5 g. of D-mannitol tribenzeneboronate and 50 ml. of water was heated on a steam-bath for 2 hr., and then cooled and extracted twice with 25-ml. portions of ether. The combined ether solution was dried over anhydrous sodium sulfate and evaporated. The residue was recrystallized twice from toluene to give 0.20 g. (48%) of benzeneboronic acid, m.p. 215–217°, alone or admixed with an authentic sample.

A mixture of 0.5 g. of D-mannitol tribenzeneboronate, 30 ml. of 10% hydrochloric acid and 30 ml. of ether was agitated, and the ether phase separated. The aqueous phase was re-extracted with 15 ml. of ether. The ether solution yielded 0.34 g. (82%) of benzeneboronic acid, m.p. 215–217°.

Rotations (25°, D-line, *c* 1.0) of D-mannitol tribenzeneboronate in various solutions were measured and the following data obtained: (solvent, rotation) anhydrous acetone, +50°; anhydrous pyridine, +58°; moist acetone, 0°; moist pyridine, 0°; absolute ethanol and acetone (1:1, by vol.), +48°.

SALT LAKE CITY 12, UTAH

(11) Knoll and Co., German Patent 105,240, Feb., 1898; *Chem. Zentr.*, **71I**, 270 (1900).