Substituted Styrenes. VII. The Syntheses and Some Reactions of the Vinylbenzeneboronic Acids

WESLEY J. DALE AND JAMES E. RUSH

Department of Chemistry, University of Missouri, Columbia, Missouri

Received February 12, 1962

Convenient methods have been devised for the syntheses of the isomeric vinylbenzeneboronic acids. Reactions providing the corresponding boroxins, 2,2′-iminodiethyl vinylbenzeneboronates, and vinylphenols, are also described.

Preliminary to an investigation of the electronic and steric effects exhibited by the boronic acid moiety upon the double bond of a substituted styrene, it was necessary to devise practical and convenient methods for the syntheses of these compounds.

The synthesis of *p*-vinylbenzeneboronic acid (I) has been reported by several workers.[1–5] Cazes[1] prepared I from the reaction of *p*-vinylphenylmagnesium bromide with methyl borate in 75% yield; Normant and Braun[2] prepared I in 80% yield in a similar manner from *p*-chlorostyrene, and Lennarz and Snyder[3] recently reported the preparation of I from both *p*-bromo- and *p*-chlorostyrene, *via* the Grignard reagent, in 20% yield. *p*-Vinylbenzeneboronic acid has also been obtained from the reaction of *p*-vinylphenylmagnesium chloride with butyl borate[4] and by the dehydrobromination of tris[*p*-(1-bromoethyl)phenyl]boroxin.[5] A modification of the method of Letsinger and Hamilton[4] was employed by the present authors and is described briefly in the Experimental.

Tris(*p*-vinylphenyl)boroxin may be prepared conveniently from I by azeotropically removing the water with toluene,[5] by filtering a carbon tetrachloride solution of I through a column of absorbent cotton,[6] by chromatographing on neutral alumina[3] or by dissolving I in warm carbon tetrachloride and separating the water layer mechanically.

The dibromide, as well as the diethanolamine ester[5] of I are easily prepared. Compounds of the latter type apparently owe their resistance to hydrolysis to the transannular coördination of the nitrogen with the boron atom.[7]

An attempt was made to prepare *m*-vinylbenzeneboronic acid (II) from *m*-vinylphenylmagnesium chloride in a manner similar to that described for preparing I, but *m*-chlorostyrene could not be induced to react with magnesium under a variety of conditions. However, *m*-bromostyrene did react with magnesium and II was successfully prepared from the reaction of *m*-vinylphenylmagnesium bromide[8] with butyl borate and was isolated in a manner analogous to that described for I.

The synthesis of *o*-vinylbenzeneboronic acid (III) by a procedure analogous to that described by Hoffmann and Thomas[5] for *p*-vinylbenzeneboronic acid met with only limited success. Letsinger and co-workers[9] have recently reported the preparation of *o*-vinylbenzeneboronic acid by dehydrobromination of tris[*o*-(1-bromoethyl)phenyl]boroxin (see also ref. 28) in 54% yield and by addition of butyl borate to *o*-vinylphenylmagnesium chloride in 3% yield.

In the present research, tris(*o*-ethylphenyl)boroxin was brominated with *N*-bromosuccinimide in carbon tetrachloride solution to give tris[*o*-(1-bromoethyl)phenyl]boroxin (IV), isolated in 75% yield. The latter compound was obtained in crystalline form only after repeated recrystallization from benzene–cyclohexane mixtures. Attempts to dehydrobrominate IV under a wide variety of conditions generally failed to give any of the desired product (III). A sample of IV, recrystallized four times from benzene–cyclohexane (1:1), when treated with freshly distilled quinoline for two minutes without external heating, gave a 32% yield of III.

When IV was treated with an ethanolic solution of potassium hydroxide, a compound with a melting point (130°) intermediate between that of IV (152°) and III (112°) was isolated. Infrared data showed this product to be *o*-(1-ethoxyethyl)benzeneboronic acid.

Treatment of IV with a hot aqueous sodium carbonate solution resulted in the formation of a low-melting solid which was insoluble in hot water. Recrystallization of this product from petroleum ether gave a white solid melting at 56–57°. This compound was first thought to be the alcohol V, although the possibility of a half ester of structure VI could not be ruled out.

Lennarz and Snyder[10] and also Torssell[11] have reported the formation of so-called boronophthalide

---

[1] J. Cazes, *Compt. rend.*, **247**, 2019 (1958).

[2] H. Normant and J. Braun, *ibid.*, **248**, 828 (1959).

[3] W. J. Lennarz and H. R. Snyder, *J. Am. Chem. Soc.*, **82**, 2169 (1960).

[4] R. L. Letsinger and S. B. Hamilton, *ibid.*, **81**, 3009 (1959).

[5] A. K. Hoffmann and W. M. Thomas, *ibid.*, **81**, 580 (1959).

[6] H. R. Snyder, M. S. Konecky, and W. J. Lennarz, *ibid.*, **80**, 3611 (1958).

[7] O. C. Musgrave and T. O. Park, *Chem. Ind.*, 1552 (1955).

[8] W. J. Dale, L. Starr, and C. W. Strobel, *J. Org. Chem.*, **26**, 2225 (1961).

[9] R. L. Letsinger, T. E. Feare, T. J. Savereide, and J. R. Nazy, *ibid.*, **26**, 1271 (1961).

[10] W. J. Lennarz and H. R. Snyder, *J. Am. Chem. Soc.*, **82**, 2172 (1960).

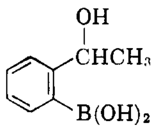
[11] K. Torssell, *Arkiv. Kemi*, **10**, 507 (1957).

TABLE I

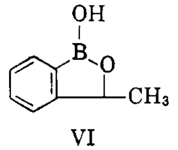
CHARACTERISTIC INFRARED ABSORPTION BANDS FOR SOME ARYLBORON COMPOUNDS

No.	Compound	Significant infrared bands (cm.$^{-1}$)[a] OH	B—O	Vinyl	Boroxin	Other
1	*o*-Ethylbenzeneboronic acid	3270	1350[b]	...	...	...
2	*m*-Ethylbenzeneboronic acid	3330	1360[b]	...	...	...
3	*p*-Ethylbenzeneboronic acid	3300	1360	...	...	...
4	*o*-Vinylbenzeneboronic acid	3300	1340[b]	1003, 915	...	...
5	*m*-Vinylbenzeneboronic acid	3220	1350[b]	995, 919	...	...
6	*p*-Vinylbenzeneboronic acid	3440	1370, 1350[c]	995, 910	...	...
7	Tris(*o*-ethylphenyl)boroxin	...	1370, 1340[c]	...	690	...
8	Tris(*m*-ethylphenyl)boroxin	...	1380, 1350[c]	...	703	...
9	Tris(*p*-ethylphenyl)boroxin	...	1350	...	680	...
10	Tris(*o*-vinylphenyl)boroxin	...	1350	990, 910	697	...
11	Tris(*m*-vinylphenyl)boroxin	...	1360, 1340[c]	995, 905	708	...
12	Tris(*p*-vinylphenyl)boroxin	...	1370	1000, 920	700	...
13	Tris[*o*-(1-bromoethyl)phenyl]boroxin	...	1370	...	692	...
14	Tris[*o*-(1,2-dibromoethyl)phenyl]boroxin	.	1370, 1335[c]	...	703	...
15	2,2′-Iminodiethyl *o*-vinylbenzeneboronate	...	1380[d]	995, 915	...	N—H, 3100; N → B, 1210
16	2,2′-Iminodiethyl *m*-vinylbenzeneboronate	...	1370[d]	1000, 908	...	N—H, 3070; N → B, 1217
17	2,2′-Iminodiethyl *p*-vinylbenzeneboronate	...	1370[d]	995, 915	...	N—H, 3110; N → B, 1215
18	*o*-(1-Ethoxyethyl)benzeneboronic acid	3333	1365	...	...	C—O stretch, 1050
19	3-Methyl-2,1-benzoxaborol-1(3*H*)-ol	3300	1365, 1345[e]	...	...	Cyclic ether, 1070; C—O stretch, 1000
20	3-Bromomethyl-2,1-benzoxaborol-1(3*H*)-ol	3300	1380, 1350[e]	...	...	Cyclic ether, 1095; C—O stretch, 987

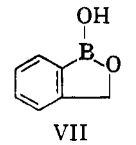
[a] All infrared spectra were obtained as Nujol mulls using a Perkin-Elmer Infracord, Model 137. [b] Broad, centered at wave length indicated. [c] Broad, split. [d] Sharp, medium intensity. [e] Sharp, split band, with longer wave length band of greater intensity.



V



VI



VII

(VII) by the alkaline hydrolysis of tris(α-bromo-*o*-tolyl)boroxin. The former authors reported infrared absorption bands for the hydroxyl and C—O groups for boronaphthalide and a number of substituted boronophthalides as falling approximately at 3300 cm.$^{-1}$ and 970 cm.$^{-1}$, respectively. The spectrum of our compound (V or VI) showed hydroxyl absorption at 3300 cm.$^{-1}$ and the absorption band attributed to C—O stretching was observed at 1000 cm.$^{-1}$. Another band, probably due to the five-membered ring ether structure,[12] was observed at 1070 cm.$^{-1}$. The two possible B—O stretching modes expected for compound VI have been assigned bands at 1345 cm.$^{-1}$ and 1365 cm.$^{-1}$. Together with the combustion analyses, these data strongly favor VI as the structure of the compound (m.p. 56–57°) which is named,[13] 3-methyl-2,1-benzoxaborol-1(3*H*)-ol.

o-Vinylbenzeneboronic acid[9] (III) was successfully prepared from *o*-vinylphenylmagnesium bromide and butyl borate in 74% yield, in a manner analogous to that described for the *meta* isomer. III forms a solid ester with diethanolamine and may be converted to tris(*o*-vinylphenyl)boroxin in the usual manner.

Attempts to prepare the dibromide derivative of III resulted in the formation of a product which is thought to be 3-bromomethyl-2,1-benzoxaborol-1(3*H*)-ol, based upon both chemical and physical data presented in the Experimental. Tris[*o*-(1,2-dibromoethyl)phenyl]boroxin was successfully prepared from tris(*o*-vinylbenzene)boroxin by the usual method.

Table I presents pertinent infrared spectra data for the aromatic boron compounds described in this paper. It can be seen that the position of the B—O band differs little from compound to compound. This band is generally broad and is the strongest band in the spectrum of both the boronic acids and the boroxins. It is significant, however, that the B—O stretching band for the 2,2′-iminodiethyl esters is relatively sharp and shows only moderate absorbance. This is likely a manifestation of the strain imposed upon the molecule by transannular coördination between the nitrogen and boron atoms. Weidmann and Zimmerman[14] have reported that the infrared spectra of a number of compounds possessing the N→B (coördination) bond exhibit bands at approximately 1200 cm.$^{-1}$ and 900 cm.$^{-1}$. We have also observed bands at these wave lengths in the spectra of compounds 15–17 (Table I) as well as in others not reported in the present work.

---

(12) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed., Methuen and Co., London, 1956, p. 104.

(13) Based on the analogous arsenic compound, 2,1-benzoxarsole; *Chem. Abstr.*, Fifth Decennial Index, 1830s (1947–1956).

(14) H. Weidmann and H. K. Zimmerman, Jr., *Ann.*, **620**, 4 (1959).

TABLE II

ULTRAVIOLET ABSORPTION CHARACTERISTICS OF SOME AROMATIC BORON COMPOUNDS

	Principal ultraviolet absorptions[a]								
	Second primary band		First primary band		Secondary band				
Compound	λ, Å.	$\epsilon \times 10^{-3}$	λ, Å.	$\epsilon \times 10^{-3}$	λ, Å.	$\epsilon \times 10^{-3}$	$\frac{\lambda_{sec}}{\lambda_{1st\ pri}}$	$\frac{\lambda_{1st\ pri}}{\lambda_{2nd\ pri}}$	$\lambda_{1st\ pri} - 2480$ Δλ
1	2030	13.2	2130	9.13	..	...	...	1.05	...
3	2020	10.5	2250	14.1	2640	0.62	1.17	1.12	...
4	2090	23.5	2470	12.3	2830	0.55	1.15	1.18	−10
5	2140	33.9	2500	12.6	2900	0.74	1.16	1.17	20
6	[b]	[b]	2590[c]	21.4[c]	2860	1.29	1.10	...	110
7	2065	70.9	2410	30.2	2810	3.47	1.17	1.16	...
10	2100	81.4	2470	41.7[d]	2900	7.25	1.17	1.18	−10
11	2160	100	2510	41.7[d]	2900	3.98	1.16	1.16	30
12	2020	69.3	2700	74.1	2990	4.17[d]	1.11	1.34	220
15	2080	24.0	2470	12.6	...	...	...	1.19	−10
16	2130	32.4	2485	11.8	...	...	...	1.17	5
17	[e]	[e]	2590	20.9	2860	1.15	1.10	...	110

[a] The spectra were obtained using a Cary Model 11 double-beam recording spectrophotometer. Ethanol (95%) was employed as solvent except for the boroxins whose spectra were obtained in dry cyclohexane. [b] Three shoulders with the following λ_{max} and log ϵ: 2045, 4.27; 2090, 4.20; 2160, 4.02. [c] Lennarz and Snyder[3] report λ_{max} 257 mμ, ϵ 23,850. [d] Shoulder. [e] Three shoulders with the following λ_{max} and log ϵ: 2050, 4.28; 2105, 4.21; 2170, 4.02.

Santucci and Gilman[15] have studied the infrared spectra of twenty-five aromatic boronic acids and have attributed a band in the 1200–1175-cm.$^{-1}$ region to the B—O stretching mode. However, the B—O stretching band in the spectrum of boric acid occurs at 1450 cm.$^{-1}$,[16] and Lappert and coworkers[17] have shown that this band appears in the 1387–1335-cm.$^{-1}$ region in the spectra of a variety of organoboron compounds. The spectra of all compounds in Table I exhibit a strong band in the 1380–1340-cm.$^{-1}$ region and, although a band in the 1200–1175-cm.$^{-1}$ region was also observed in the spectra of a majority of these compounds, it was of variable intensity, usually weak, and was not present at all in the spectra of compounds 4, 5, and 6 (Table I).

The assignment of bands in the infrared spectra of substituted boroxins has also been subject to some disagreement. Santucci and Gilman[15] suggested that the disappearance of a band at 1030–1020 cm.$^{-1}$ is indicative of boroxin formation, but a band in this region is still present in the spectra of the boroxins 9, 10, and 12 (Table I). We noted, in agreement with the observations of Snyder and co-workers,[6] that in the conversion of the acid to the boroxin, the spectrum of the boroxin showed the concurrent disappearance of the hydroxyl band and the appearance of an intense band at approximately 700 cm.$^{-1}$. Lappert and associates,[17] who attribute the band near 700 cm.$^{-1}$ to out-of-plane deformation of the boroxin ring, presented evidence which lends further support to our observations. Furthermore, both the band near 3300 cm.$^{-1}$ and that near 700 cm.$^{-1}$ are present in the spectra of mixtures of the acid and boroxin.

The principal ultraviolet absorption bands of twelve arylboron compounds are presented in Table II. The terminology of Doub and Vandenbelt[18] has been employed in distinguishing the various bands, and the correctness of these assignments may be inferred from the ratios shown in Table II.

The displacement of the first primary band in *p*-vinylbenzeneboronic acid (2590 Å.), relative to that of styrene (2480 Å.), indicates a rather significant mesomeric interaction between the groups situated *para* to one another. This interaction is most pronounced (Δλ = 220 Å.) in the boroxin. Lack of a similar displacement in the *ortho* isomers may be attributed, at least in part, to steric interference between the substituents.

It should be noted that the existence of transannular coördination between the boron and nitrogen atoms in the diethanolamine esters (compounds 15, 16, and 17) causes no change in the ultraviolet spectra of these esters in relation to the spectra of the parent acids.

Aside from reactions typical of acids, boronic acids undergo a number of transformations which result in the loss of the borono group.[19] Of particular interest was the oxidative cleavage of areneboronic acids by hydrogen peroxide, since the products of the reaction are phenols and boric acid.[20,21] In the case of the vinylbenzeneboronic acids, this reaction would provide a new route to the vinylphenols, whose syntheses have been reported earlier by rather tedious procedures.[22] When suitably modified, the procedure described by Hawthorne[23] proved to be satisfactory for the controlled deboronation of the vinylbenzeneboronic acids.

---

(15) L. Santucci and H. Gilman, *J. Am. Chem. Soc.*, **80**, 193 (1958).

(16) D. E. Bethell and N. Sheppard, *Trans. Faraday Soc.*, **51**, 9 (1955).

(17) D. W. Aubrey, M. F. Lappert, and H. Pyszora, *J. Chem. Soc.*, 1931 (1961).

(18) L. Doub and J. M. Vandenbelt, *J. Am. Chem. Soc.*, **69**, 2714 (1947).

(19) M. F. Lappert, *Chem. Rev.*, **56**, 994 (1956).

(20) A. D. Ainley and F. Challenger, *J. Chem. Soc.*, 2171 (1930).

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

(22) W. J. Dale and H. E. Hennis, *ibid.*, **80**, 3645 (1958).

(23) M. F. Hawthorne, *J. Org. Chem.*, **22**, 1001 (1957).

Thus, the vinylbenzeneboronic acids were suspended, or partially dissolved, in a petroleum ether–ethyl acetate solution (4:1 by volume)[22] and treated with aqueous hydrogen peroxide. Excess peroxide was destroyed with ferrous ammonium sulfate solution, and the solvent was then removed in the cold under a nitrogen atmosphere and reduced pressure to obtain the isomeric vinylphenols.

The results of our continuing investigation of various reactions of the vinylbenzeneboronic acids and related compounds will be reported in subsequent papers in this series.

Experimental[24]

Preparation of Materials.—*o*- and *m*-bromostyrene were prepared by vapor phase dehydration of *o*- and *m*-bromo-α-methylbenzyl alcohol in the presence of alumina under reduced pressure. The alcohols were prepared from the reaction of the appropriate aldehyde with methylmagnesium iodide. *p*-Chlorostyrene was prepared from *p*-dichlorobenzene as described by Ramsden and Leebrick.[25] *n*-Butyl borate was prepared from *n*-butyl alcohol and boric oxide (B_2O_3) and distilled immediately before use. Tetrahydrofuran was distilled from lithium aluminum hydride just before use. Quinoline was purified as described by Vogel.[26]

***p*-Vinylbenzeneboronic Acid.**—This compound was prepared in a manner similar to that of Letsinger and Hamilton.[4] *p*-Vinylphenylmagnesium chloride was prepared by the method of Ramsden and Leebrick[25] from 138.6 g. (1 mole) of freshly distilled *p*-chlorostyrene and 24.3 g. (1 g.-atom) of magnesium. The Grignard reagent was then added rapidly, dropwise, to a stirred solution of 300 g. (1.3 moles) of butyl borate in 600 ml. of anhydrous ether cooled to −70°. After addition was complete, the reaction mixture was allowed to warm to room temperature during a 6-hr. period.

The reaction mixture was then decomposed with 3 *M* hydrochloric acid, the layers were separated and the aqueous phase was extracted with one 100-ml. portion of ether. The solvent was removed under reduced pressure from the combined ether layers. One liter of water was then added to the residue and the mixture was distilled under reduced pressure to remove the butanol; water was added as necessary to maintain a volume of 1 l. When removal of the butanol was virtually complete, distillation was stopped and the resulting slurry was transferred to a beaker and warmed until solution of the solid was attained. The aqueous phase was then separated by decantation from a brown oil [consisting mainly of bis(*p*-vinylphenyl)borinic acid]. The hot solution was cooled in an ice bath and the white, crystalline solid which separated was collected on a suction filter. The air-dried solid weighed 102.7 g. (69.5%), m.p. 189–191° dec. An additional 9.6 g. (6.5%) of product was obtained by extracting the aqueous filtrate with ether, evaporating the combined extracts to dryness, and recrystallizing the residue from about 100 ml. of hot water. One additional recrystallization gave white plates, m.p. 190–191° dec.

Anal.[1–4,27] Calcd. for $C_8H_9BO_2$: C, 64.93; H 6.13. Found: C, 65.28; H, 6.24.

The dibromide derivative was prepared in carbon tetrachloride solution and recrystallized from aqueous acetone to give fine white needles, m.p. 198–200°.

Anal. Calcd. for $C_8H_9BO_2Br_2$: C, 31.21; H, 2.95. Found: C, 31.21; H, 2.85.

2,2′-Iminodiethyl *p*-vinylbenzeneboronate was prepared by the method of Hoffmann and Thomas.[5] The product was recrystallized from acetone to give white needles, m.p. 235–236° (lit.,[5] m.p. 236–237° dec.).

Tris(*p*-vinylphenyl)boroxin was prepared by the method of Snyder, Konecky, and Lennarz.[6] Recrystallization from carbon tetrachloride gave long white needles, m.p. 195° (lit.,[5] m.p. 195–196°).

***p*-Vinylphenol from *p*-Vinylbenzeneboronic Acid.**—A modification of the deboronation procedure of Hawthorne[23] was employed. To a stirred suspension of 25.0 g. (0.167 mole) of *p*-vinylbenzeneboronic acid in a solution of petroleum ether and ethyl acetate (4:1 by volume),[22] maintained at 22° by means of a water bath, was added 100 ml. of a 5.67% aqueous solution (0.167 mole) of hydrogen peroxide at the rate of 1 drop/sec. The progress of the reaction was noted by the disappearance of the suspended solid. When the addition of the peroxide was complete, the reaction mixture was stirred for 10 min., filtered, and the layers separated. The aqueous phase was extracted once with 15 ml. of the solvent, the combined organic extracts were shaken with ferrous ammonium sulfate solution, and the organic layer dried over anhydrous magnesium sulfate. The solvent was removed, in the cold, under reduced pressure and a nitrogen atmosphere. The white crystalline solid which separated weighed 15.0 g. (74%). Recrystallization of the product from petroleum ether afforded fine white needles of *p*-vinylphenol, m.p. 71–71.5° (lit.,[22] m.p. 71–72°).

The benzoate derivative, prepared under Schotten-Baumann conditions, was recrystallized from aqueous ethanol to give white needles, m.p. 74.5–76° (lit.,[22] m.p. 75.5–76°).

The tosylate derivative, prepared under the same conditions, was recrystallized from aqueous ethanol to afford white needles, m.p. 68° (lit.,[22] m.p. 68–68.5°).

***m*-Vinylbenzeneboronic Acid.**[28]—*m*-Vinylphenylmagnesium bromide was prepared, as described by Dale, Starr, and Strobel,[8] from 36.6 g. (0.20 mole) of freshly distilled *m*-bromostyrene and 4.88 g. (0.21 g.-atom) of magnesium. The Grignard reagent was then added rapidly, dropwise, to a solution of 57.9 g. (0.25 mole) of butyl borate in 200 ml. of anhydrous ether cooled to −70°. After addition was complete, the reaction mixture was allowed to warm to room temperature during a 4-hr. period.

The reaction mixture was then decomposed with 3 *M* hydrochloric acid and the product was isolated by a procedure analogous to that described for *p*-vinylbenzeneboronic acid. The air-dried product weighed 26.1 g. (88.3%), m.p. 143–145°. One additional recrystallization from hot water afforded white plates, m.p. 144–145°.

Anal. Calcd. for $C_8H_9BO_2$: C, 64.93; H, 6.13. Found: C, 64.93; H, 6.21.

The dibromide derivative was recrystallized from aqueous acetone, which afforded white needles, m.p. 196–197.5°.

Anal. Calcd. for $C_8H_9BO_2Br_2$: C, 31.21; H, 2.95; Br, 51.93. Found: C, 31.38; H, 3.12; Br, 51.12.

Tris(*m*-vinylphenyl)boroxin.—This compound was prepared in a manner similar to that used for the *para* isomer. From 1.0 g. (0.0068 mole) of *m*-vinylbenzeneboronic acid there was obtained, after two recrystallizations from carbon tetrachloride, 0.45 g. (50.0%) of white needles, m.p. 146–146.5°.

Anal. Calcd. for $C_{24}H_{21}B_3O_3$: C, 73.93; H, 5.43. Found: C, 72.76; H, 5.81.

---

(24) All melting points are uncorrected. The carbon, hydrogen, bromine, and nitrogen analyses were performed by Drs. Weiler and Strauss, Oxford, England.

(25) H. E. Ramsden and J. R. Leebrick, *J. Org. Chem.*, **23**, 935 (1958).

(26) A. I. Vogel, "Textbook of Practical Organic Chemistry," Longmans, Green and Co., London, 1956, p. 829.

(27) Since no completely satisfactory analytical data have been reported for this compound, we include such data.

(28) Hoffmann and co-workers [A. K. Hoffmann, S. J. Groszos, and W. M. Thomas, U.S. Patent 2,934,556, April 26, 1960; *Chem. Abstr.*, **54**, 17327 (1960)] have reported the preparation of *o*-, *m*-, and *p*-vinylbenzeneboronic acid by the dehydrobromination of the corresponding tris-[*o*-, *m*-, and *p*-(1-bromoethyl)phenyl]boroxin. The preparation of these acids *via* the Grignard reagent has also been reported [U.S. Borax and Chemical Corp., British Patent 871,185, June 21, 1961; *Chem. Abstr.*, **55**, 24678 (1961)]. No yields, physical properties, or analytical data are given.

2,2′-Iminodiethyl *m*-Vinylbenzeneboronate.—A mixture of 1.5 g. (0.01 mole) of *m*-vinylbenzeneboronic acid, 1.1 g. (0.01 mole) of 2,2′-iminodiethanol and 40 ml. of toluene was heated at reflux for 1 hr., after which the mixture was cooled and filtered. Recrystallization of the product from acetone gave 2.13 g. (98.0%) of white needles, m.p. 197–198°.

Anal. Calcd. for $C_{12}H_{16}BO_2N$: C, 66.39; H, 7.42; N, 6.45. Found: C, 66.59; H, 7.48; N, 6.73.

***m*-Vinylphenol from *m*-Vinylbenzeneboronic Acid.**—*m*-Vinylbenzeneboronic acid (3.9 g., 0.026 mole) was suspended in 35 ml. of petroleum ether–ethyl acetate solution (4:1) in a 50-ml. separatory funnel and 19 ml. of 10% aqueous hydrogen peroxide was added. The mixture was shaken for 10 min., after which the layers were separated. The organic layer was shaken with ferrous ammonium sulfate solution and then dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and a nitrogen atmosphere and the residue was distilled under reduced pressure to give 1.0 g. (32%) of a pale yellow liquid whose infrared spectrum was consistent with that of *m*-vinylphenol.

The phenylurethan derivative, prepared according to Shriner, Fuson, and Curtin,[29] was recrystallized from petroleum ether–benzene (3:1) to give heavy white needles, m.p. 131–131.5°.

Anal. Calcd. for $C_{15}H_{13}NO_2$: C, 75.30; H, 5.48; N, 5.85. Found: C, 75.56; H, 5.42; N, 6.04.

***o*-Ethylbenzeneboronic Acid.**—*o*-Ethylphenylmagnesium bromide, prepared from 185.1 g. (1 mole) of *o*-bromoethylbenzene and 24.3 g. (1 g.-atom) of magnesium in 500 ml. of anhydrous ether, was added rapidly, dropwise, to a stirred solution of 300 g. (1.3 moles) of butyl borate in 500 ml. of ether cooled to −70°. The reaction mixture was allowed to warm to room temperature and was then decomposed by the addition of 400 ml. of 3 *M* hydrochloric acid. The product was isolated by a procedure analogous to that described for *p*-vinylbenzeneboronic acid. Recrystallization from hot water afforded 103.0 g. (68.8%) of *o*-ethylbenzeneboronic acid as white needles, m.p. 115–117°.

Anal.[9,27] Calcd. for $C_8H_{11}BO_2$: C, 64.05; H, 7.39. Found: C, 63.98; H, 7.23.

Tris(*o*-ethylphenyl)boroxin.—A mixture of 73.0 g. (0.49 mole) of *o*-ethylbenzeneboronic acid and 500 ml. of carbon tetrachloride was heated to effect solution, the layers were separated and the carbon tetrachloride solution was reduced in volume to about 150 ml. Cooling in an ice bath caused the separation of 64.2 g. (99.5%) of crystalline tris(*o*-ethylphenyl)boroxin. A sample recrystallized from carbon tetrachloride gave white needles m.p. 117.5–118.5° (lit.,[9] m.p. 117–117.5°).

Anal.[9,27] Calcd. for $C_{24}H_{27}B_3O_3$: C, 72.80; H, 6.87. Found: C, 72.69; H, 6.78.

Tris[*o*-(1-bromoethyl)phenyl]boroxin.—A procedure similar to that of Letsinger and co-workers[9] was employed. Tris(*o*-ethylphenyl)boroxin (19.8 g., 0.05 mole) was dissolved in 500 ml. of anhydrous carbon tetrachloride and 27.0 g. (0.15 mole) of *N*-bromosuccinimide was added. The mixture was heated to reflux and 0.3 g. of benzoyl peroxide was added. After completion of reaction, the succinimide was removed by filtration, washed with a small amount of the solvent and the filtrate was then concentrated under reduced pressure. Cooling the remaining solution caused 23.5 g. (74.5%) of a cream colored product to separate. A sample, recrystallized four times from 1:1 benzene–cyclohexane, gave a white crystalline material, m.p. 152–152.5° (lit.,[9] m.p. 148.5–150°).

Anal.[9,27] Calcd. for $C_{24}H_{24}B_3O_3Br_3$: C, 45.56; H, 3.82; Br, 37.90. Found: C, 45.45; H, 4.14; Br, 36.80.

Dehydrobromination of Tris[*o*-(1-bromoethyl)phenyl]boroxin. A. Ethanolic Potassium Hydroxide.—Tris[*o*-(1-bromoethyl)phenyl]boroxin (2.0 g., 0.0032 mole) was dissolved in 15 ml. of absolute ethanol and 10 ml. of an ethanolic potassium hydroxide solution (0.0096 mole of potassium hydroxide) was added. A precipitate of potassium bromide formed immediately. The solution was filtered, neutralized with acid and evaporated to about one half its original volume. Water (15 ml.) was added and the solution was further evaporated. Cooling the remaining solution in an ice bath caused the separation of 1.57 g. of a tan crystalline material. Recrystallization from aqueous acetone afforded white needles, m.p. 129–131°.

Anal. Calcd. for $C_{10}H_{15}BO_3$: C, 61.89; H, 7.78. Found: C, 61.75; H, 7.75.

It was evident from the method of synthesis, the infrared spectrum, and the elemental analysis that the compound is *o*-(1-ethoxyethyl)benzeneboronic acid.

B. **Quinoline.**—Tris[*o*-(1-bromoethyl)phenyl]boroxin (2.0 g., 0.0032 mole) was added to 4.0 ml. of freshly distilled quinoline contained in a 50-ml. Erlenmeyer flask. The mixture, which warmed spontaneously to *ca.* 70°, was swirled for 2 min. and then 20 ml. of a 3 *M* hydrochloric acid solution was added. The resultant solution was extracted with four 25-ml. portions of ether, the ether extracts were combined, and the ether was removed by evaporation. The residue was recrystallized from hot water to give 0.45 g. (32%) of white plates. A further recrystallization from hot water gave pure *o*-vinylbenzeneboronic acid[28] as rectangular plates, m.p. 111–112° (lit.,[9] m.p. 108–109°).

Anal.[9,27] Calcd. for $C_8H_9BO_2$: C, 64.93; H, 6.13. Found: C, 64.61; H, 6.38.

C. **Aqueous Sodium Carbonate.**—A solution of 1.23 g. (0.012 mole) of sodium carbonate and 30 ml. of water was heated to 75° and 3.65 g. (0.0058 mole) of crude IV was added. After carbon dioxide ceased to be evolved, the solution was acidified and filtered. The aqueous layer was separated from a brown oil and cooled in an ice bath but no organic material could be isolated from this layer. The oil crystallized on standing for 36 hr. in the cold, giving 2.48 g. of solid melting at 52–56°. After two recrystallizations from petroleum ether, the compound was obtained as heavy white needles, m.p. 56–57°, presumably 3-methyl-2,1-benzoxaborol-1(3*H*)-ol.

Anal. Calcd. for $C_8H_9BO_2$: C, 64.93; H, 6.13. Found: C, 65.06; H, 6.14.

***o*-Vinylbenzeneboronic Acid.**[28]—*o*-Vinylbenzeneboronic acid was also prepared *via* a Grignard reagent, using a procedure similar to that of Letsinger and co-workers,[9] but with modifications which provided higher yields. *o*-Vinylphenylmagnesium bromide,[8] prepared from 82.5 g. (0.45 mole) of *o*-bromostyrene and 10.9 g. (0.45 g.-atom) of magnesium in 250 ml. of tetrahydrofuran, was added dropwise at a rapid rate to a solution of 127 g. (0.55 mole) of butyl borate in 300 ml. of anhydrous ether cooled to −70°. After addition was complete, the reaction mixture was allowed to warm to room temperature over a period of 6 hr.

The reaction mixture was then decomposed with 3 *M* hydrochloric acid, and the product was isolated in the same manner as that described for the *para* isomer. The air-dried product weighed 49.0 g. (73.6%), m.p. 108–109°. An additional recrystallization from hot water gave white plates, m.p. 111–112°.

Tris(*o*-vinylphenyl)boroxin.—*o*-Vinylbenzeneboronic acid (1.0 g., 0.0068 mole) was dissolved in 25 ml. of warm carbon tetrachloride and the resultant solution was filtered through a pad of absorbent cotton. The filtrate was evaporated to about 10 ml. and cooled in an ice bath. The white needles which separated were collected on a filter; yield, 0.80 g. (91%), m.p. 94–96°. Recrystallization of a small sample from cyclohexane did not raise the melting point.

Anal. Calcd. for $C_{24}H_{21}B_3O_3$: C, 73.93; H, 5.43. Found: C, 73.57; H, 6.21.

This compound yellows on standing (even in a desiccator) for as little as 48 hr. Although the infrared spectrum of freshly prepared tris(*o*-vinylphenyl)boroxin exhibits well resolved bands, the bands in the spectrum of the yellow

---

(29) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 265.

material are ill-defined and the compound is assumed to be polymeric.

Tris[*o*-(1,2-dibromoethyl)phenyl]boroxin.—*o*-Vinylbenzeneboronic acid (3.0 g.) was dissolved in warm carbon tetrachloride and the water layer which formed was separated. The carbon tetrachloride solution was reheated, filtered, and the filtrate was cooled to room temperature. Bromine was then added until a faint color persisted. The solvent was removed and the residue was recrystallized from benzene–petroleum ether (1:3) to give white crystalline material (4.0 g., 68%), m.p. 172–174°. Two additional recrystallizations afforded material melting at 173.5–175.5°. The absence of a band in the 3500–3000-cm.$^{-1}$ region and the presence of a strong band at 704 cm.$^{-1}$ in the infrared spectrum of this compound is consistent with the boroxin structure.

Anal. Calcd. for $C_{24}H_{21}B_3O_3Br_6$: C, 33.16; H, 2.43; Br, 55.15. Found: C, 33.33; H, 2.41; Br, 50.50.

This compound reacted immediately with alcoholic silver nitrate and with sodium iodide in acetone.

3-Bromomethyl-2,1-benzoxaborol-1(3*H*)-ol. A. From Attempted Preparation of *o*-(1,2-Dibromoethyl)benzene boronic Acid.—*o*-Vinylbenzeneboronic acid, suspended in carbon tetrachloride, was treated with a solution of bromine in carbon tetrachloride in the usual manner. The solvent was removed, the residue was dissolved in aqueous acetone and the resultant solution was allowed to stand 72 hr. at room temperature. The crystals which separated were collected on a filter and recrystallized twice from aqueous acetone; m.p. 100.5–101.5°.

Anal. Calcd. for $C_8H_8BO_2Br$: C, 42.34; H, 3.55; Br, 35.22. Found: C, 41.95, 42.74; H, 3.91, 3.61; Br, 34.95.

The above carbon and hydrogen values do not correspond to the structure of *o*-(1,2-dibromoethyl)benzeneboronic acid (C, 31.21; H, 2.95; Br, 51.93, calculated for $C_8H_9BO_2Br_2$) but do correspond to those of 3-bromomethyl-2,1-benzoxaborol-1(3*H*)-ol, whose infrared spectrum and chemical properties are similar to those of 3-methyl-2,1-benzoxaborol-1(3*H*)-ol, described earlier. Thus, both the latter compound and its above bromo derivative are soluble in sodium hydroxide solution but not in sodium bicarbonate solution and neither is soluble in hot or cold water. The 3-bromomethyl-2,1-benzoxaborol-1(3*H*)-ol failed to react with either ethanolic silver nitrate solution or with sodium iodide in acetone.

B. From Tris[*o*-(1,2-dibromoethyl)phenyl]boroxin.—Although tris[*o*-(1,2-dibromoethyl)phenyl]boroxin was recovered unchanged from an aqueous acetone solution after 6 hr., a good yield of the benzoxaborole was obtained from the boroxin in the following manner. Two grams of the above boroxin was dissolved in 75 ml. of aqueous acetone (2:1), and the solution was allowed to stand at room temperature for 132 hr. The solution was then extracted with ether, the extracts were combined, and the solvent was removed under reduced pressure. The crystalline solid which remained (1.4 g., 91%) was recrystallized twice from benzene–petroleum ether (2:1) to give white needles, m.p. 100.5–101.5°. The infrared spectrum of this material was identical with that of 3-bromomethyl-2,1-benzoxaborol-1(3*H*)-ol prepared above.

2,2′-Iminodiethyl *o*-Vinylbenzeneboronate.—A mixture of 1.5 g. (0.01 mole) of *o*-vinylbenzeneboronic acid, 1.1 g. (0.01 mole) of 2,2′-iminodiethanol and 30 ml. of toluene was heated at reflux for 45 min., then cooled. The white crystalline solid (2.04 g., 94%) was collected on a filter, m.p. 199–201°. A sample recrystallized twice from acetone, melted at 201–202.5°.

Anal. Calcd. for $C_{12}H_{16}BO_2N$: C, 66.39; H, 7.42; N, 6.45. Found: C, 66.09; H, 7.70; N, 6.41.

***o*-Vinylphenol from *o*-Vinylbenzeneboronic Acid.**—Vinylbenzeneboronic acid (3.90 g., 0.026 mole), 35 ml. of petroleum ether–ethyl acetate (4:1) and 15.7 ml. of 5.67% aqueous hydrogen peroxide were placed in a 50-ml. separatory funnel and the mixture was shaken for 10 min. The layers were separated and the organic layer was shaken with ferrous ammonium sulfate solution. The organic layer was dried over anhydrous magnesium sulfate and the product was isolated in the usual manner. Distillation of the residual oil gave 1.15 g. (37%) of a pale yellow liquid which solidified on cooling. The infrared spectrum of this compound was identical with the spectrum of authentic *o*-vinylphenol.[30]

The tetrabromide derivative, 2,4-dibromo-6-(1,2-dibromoethyl)phenol, was prepared as described by Fries and Fickewirth[31] and recrystallized from benzene–petroleum ether (1:3) to give clumps of white crystals, m.p. 104–105° (lit.,[31] m.p. 105°).

---

(30) H. E. Hennis, thesis, Doctor of Philosophy, University of Missouri, 1956.

(31) K. Fries and G. Fickewirth, *Ber.*, **41**, 367 (1908).