Anal. Calcd. for $C_8H_8B_2O_4$: C, 50.61; H, 4.25; B, 11.40. Found: C, 50.29; H, 4.39; B, 11.21.

Increasing the amount of N-bromosuccinimide used to 2 equiv. reduced the yield of II.

Isolation of 5-Bromo-1,4-xylene-2-boronic Acid.—In the fractionation of the butyl ester of 1,4-xylene-2,5-diboronic acid a considerable amount of material, lower boiling than the required ester, was obtained. From this was isolated, by hydrolysis and several crystallizations, 5-bromo-1,4-xylene-2-boronic acid anhydride, m.p. 228°.

Anal. Calcd. for C_8H_8BBrO: C, 45.57; H, 3.82; Br, 37.90. Found: C, 45.58; H, 3.88; Br, 37.72.

Preparation of 4-Bromo-5-hydroxymethylboronophthalide.—5-Bromo-1,4-xylene-2-boronic acid anhydride (4.34 g.) in boiling carbon tetrachloride (600 ml.) was treated with N-bromosuccinimide (7.5 g., 2 equiv.) in small portions, under ultraviolet irradiation. The solution was cooled, filtered, and shaken with dilute potassium hydroxide solution; the alkaline extract was acidified and the product was extracted with ether. Ether was distilled off and the residue was crystallized from aqueous ethanol after treatment with Darco, yield 0.64 g. (13%). Recrystallization and drying at 100° (0.1 mm.) gave white needles, m.p. 279–280°.

Anal. Calcd. for $C_8H_8BBrO_3$: C, 39.56; H, 3.32. Found: C, 39.71; H, 3.37.

Preparation of 5-Methylboronophthalide.—1,4-Xylene-2-boronic acid anhydride (6.6 g.), m.p. 196°, in boiling carbon tetrachloride (700 ml.) was treated with N-bromosuccinimide (8.9 g., 1 equiv.) under ultraviolet irradiation. After filtration the solution was cooled and shaken with dilute potassium hydroxide solution which, on acidification, gave 5-methylboronophthalide, 3.42 g. (46%), m.p. 111–113°. Recrytallization from water raised the melting point to 115° although softening still began at 111°.

Anal. Calcd. for $C_8H_9BO_2$: C, 64.93; H, 6.13. Found: C, 65.17; H, 6.27.

Reaction of 5-Methylboronophthalide with N-Bromosuccinimide.—5-Methylboronophthalide (1.48 g.) in boiling carbon tetrachloride was stirred and heated with N-bromosuccinimide (1.8 g., 1 equiv.) under ultraviolet irradiation for 2 hr. The solution was filtered, cooled, and treated with dilute alkali; the extract was acidified and the product was taken up in ether. After evaporation of the ether, the residue was crystallized from water after treatment with Darco, then from chloroform–carbon tetrachloride, and twice more from water, yielding needles, m.p. 191–193.5°, after drying over phosphorus pentoxide.

Anal. Calcd. for $C_8H_9BO_3$: C, 58.60; H, 5.53. Found: C, 58.74; H, 5.58.

The infrared spectrum of this compound is very similar to that of *o*-formylbenzeneboronic acid,[9] having a strong absorption band at 1660 cm.$^{-1}$ (Nujol mull). The p.m.r. spectrum, in dioxane, shows peaks at $\tau = 0.06$ (s), 2.32 (m), and 7.60 (s) p.p.m., with approximate relative areas 1:5:3. These were attributed to formyl, aromatic plus hydroxyl, and methyl protons, respectively.

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(9) A. J. Reedy, Ph.D. Thesis, University of Illinois (1957).

Monoglucose Derivatives of Gentisic Acid

A. ZANE AND S. H. WENDER

The text below was inadvertently omitted from the Note that was published on p. 2078 of the July, 1964, issue.

Gentisic Acid 5-β-D-Glucopyranoside (I).—Methyl 2-hydroxy-5-*O*-β-D-glucopyranosyloxybenzoate[2] (4.3 g., 0.013 mole) was dissolved in barium hydroxide solution (210 ml., 0.43 *N*) and let stand for 5 hr. at room temperature. The reaction mixture then was neutralized with an equivalent amount of oxalic acid solution. After 1 hr., the precipitate was filtered off, and the clear, pale yellow filtrate was concentrated *in vacuo* at 38° until crystallization occurred. The product was filtered off, washed with a small amount of cold water, and then air-dried to give white, needle-like crystals (3.8 g., 92%), m.p. 97–100°. Crystallization from hot water (30 ml.) produced white needles, m.p. 98–100°.

Anal. Calcd. for $C_{13}H_{16}O_9 \cdot 2H_2O$ (352.29): C, 44.32; H, 5.72. Found: C, 44.51; H, 5.69.

Drying a sample for 6 hr. over phosphorus pentoxide at 110° *in vacuo* produced a semiopaque material, m.p. 126–128°.

Anal. Calcd. for $C_{13}H_{16}O_9 \cdot 1.5H_2O$ (343.28): C, 45.48; H, 5.58. Found: C, 45.21; H, 5.60.

R_f values in the BAW, 2% acetic acid, and IBFW systems were 0.36, 0.81, and 0.24, respectively. The water content of the dried product was 7.3% as obtained by a coulometric Karl Fischer method.[4]

Gentisic Acid 2-β-D-Glucopyranoside (II).—Methyl 5-hydroxy-2-*O*-β-D-glucopyranosyloxybenzoate[2] (10 g., 0.03 mole) was similarly treated with barium hydroxide solution (500 ml.) and oxalic acid. The precipitate was filtered off and, after concentration *in vacuo*, crystallization occurred. The solid material was filtered off and discarded, and the filtrate was taken to dryness *in vacuo*. The resulting solid was dissolved in warm ethyl alcohol (120 ml.) and filtered; the filtrate was concentrated to half volume and then added to an excess of ethyl acetate (1500 ml.). The resulting solution was concentrated to half volume, and the white product was filtered off, washed with ethyl acetate, and then air-dried to yield a white powder (3.3 g., 35%), m.p. 155–156°. Crystallization from hot water produced very fine needles, m.p. 129–131°. Subsequent recrystallizations from water did not raise this last melting point.

Anal. Calcd. for $C_{13}H_{16}O_9 \cdot H_2O$ (334.27): C, 46.71; H, 5.43. Found: C, 46.72; H, 5.42.

R_f values in BAW, 2% acetic acid, and IBFW were 0.40, 0.83, and 0.15, respectively. The water content of the product was 6.4% obtained by a coulometric Karl Fischer method.[4]

Acknowledgment.—The microanalyses were performed by Galbraith Laboratories, Knoxville, Tennessee, and the water analyses were done by Mr. Ronald Grigsby, University of Oklahoma. This work was supported in part by a National Institutes of Health Grant (GM-08276).

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(4) A. S. Meyer Jr. and C. M. Boyd, *Anal. Chem.*, **31**, 215 (1959).