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Organoboron Compounds. Part VIII.¹ Aliphatic and Aromatic Di**boronic Acids**

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Diboronic acids $(HO)_2B \cdot R \cdot B(OH)_2$ (where R = polymethylene, arylene, or thiophen-2,5-diyl) are prepared by reactions of methyl borate with difunctional Grignard reagents and are characterised by the formation of cyclic esters with various diols. The polymethylenediboronic acids are much more resistant to aerial oxidation than are the corresponding alkylboronic acids. All the diboronic acids undergo dehydration to the corresponding polymeric anhydrides, the aromatic compounds requiring temperatures >230°. Reactions which result in deboronation or in the formation of amine complexes are described. Thiophen-2,5-diyldiboronic acid undergoes hydrogenolysis on treatment with Raney nickel to give tetramethylenediboronic acid.

DIBORONIC acids (HO)₂B·R·B(OH)₂ are of potential interest in both cancer therapy 2 and the formation of polymeric materials.³ We have therefore examined the preparation and properties of a number of such aliphatic and aromatic acids. The dichlorides or dibromides (I—VII; Y = Cl or Br) reacted readily with magnesium in tetrahydrofuran⁴ to form the corresponding difunctional Grignard reagents, which when treated with ethereal trimethyl borate at -70° , with subsequent acidification, gave satisfactory yields (38-63%) of the diboronic acids [I-VII; $Y = B(OH)_2$]. In contrast the reaction of trimethyl borate with the dilithium compound derived from the dibromide (III; Y = Br) gave a poor (13%) yield of the corresponding diboronic acid. All the diboronic acids lose water when heated and were therefore characterised by the formation of the corresponding bis-2,2-dimethyltrimethylene and bis-2,2'-iminodiethyl diboronates [I-VII; Y = (VIII) and (IX) respectively] or of related derivatives prepared from o-hydroxybenzyl alcohol, o-phenylenediamine, or catechol.

¹ Part VII, R. A. Bowie and O. C. Musgrave, preceding paper.
² A. H. Soloway, Progr. Boron Chem., 1964, 1, 203.
³ A. L. McCloskey, in 'Inorganic Polymers,' ed. F. G. A. Stone

The polymethylenediboronic acids [I; n = 4, 5, 6, or 10, $Y = B(OH)_2$, some of which have been prepared by a much less convenient route,⁵ differ in behaviour from the alkylboronic acids ⁶ in several ways. They are not so easily dehydrated and are unaffected by prolonged exposure to air or dry oxygen. Whereas the alkylboronic acids are too weak to be titrated against alkali in the presence of mannitol, the diboronic acids can be titrated without difficulty, behaving as dibasic acids. The alkaline hydrogen peroxide oxidation of decamethylenediboronic acid [I; n = 10, $Y = B(OH)_2$] gave decane-1,10-diol so confirming the structure of this acid.

Dehydration of tetramethylenediboronic acid [I; n = 4, $Y = B(OH)_2$ either by heating at $130^{\circ}/0.1$ torr or by boiling with toluene gave the corresponding dianhydride $(OB \cdot [CH_2]_4 \cdot BO)_n$ as an involatile glass which, although unaffected by being heated at 250° in vacuo. slowly decomposed on exposure to air, and which on treatment with water regenerated the

and W. A. G. Graham, Academic Press, New York, 1962, p. 159. ⁴ H. Heaney, Organometallic Chem. Rev., 1966, **1**, 27.

⁵ L. I. Zakharkin and A. I. Kovredov, (a) Zhur. obshchei *L. H. D. C. Barnar Kin and A. H. H. Herberger, (a) Datas Costenet Khim.*, 1962, **32**, 1421; 1966, **36**, 2153 (*Chem. Abs.*, 1963, **58**, 4589c; 1967, **66**, 116,097d); (b) *Izvest. Akad. Nauk S.S.S.R.*, *Otdel khim. Nauk*, 1962, 357 (*Chem. Abs.*, 1962, **57**, 12,519f); (c) *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1968, 1070 (*Chem.*

 ^(d) Librar, 1968, 69, 106,781v).
 ⁶ H. R. Snyder, J. A. Kuck, and J. R. Johnson, J. Amer. Chem. Soc., 1938, 60, 105.

diboronic acid. The apparent ' melting points ' of these diboronic acids depend on the rate of heating. Tetramethylenediboronic acid melts at 177-179° when heated rapidly but at lower temperatures when heated slowly. The i.r. absorption spectrum of each of the acids shows a strong doublet at 3280 and 3410 cm.⁻¹. The first of these bands may be attributed to the H-O stretching mode of hydrogen-bonded hydroxy-groups. A single absorption band in a similar position is shown by methylboronic acid⁷ (at 3295 cm.⁻¹) and by butylboronic acid (at 3235 cm.⁻¹), and the latter has been shown⁸ to be hydrogen-bonded. The second band of the doublet, which is not shown by alkylmonoboronic

$$\begin{array}{ccc} \mathbf{Y} \cdot [\mathbf{CH}_2]_n \cdot \mathbf{Y} & \not{p} \cdot \mathbf{Y} \cdot \mathbf{C}_6 \mathbf{H}_4 \cdot \mathbf{Y} \\ (\mathbf{I}) & (\mathbf{II}) \\ \\ \not{p} \cdot \mathbf{Y} \cdot \mathbf{C}_6 \mathbf{H}_4 \cdot \mathbf{C}_6 \mathbf{H}_4 \cdot \mathbf{Y} - \not{p} & & & & & & \\ (\mathbf{III}) & & & & & & & \\ (\mathbf{III}) & & & & & & & \\ (\mathbf{IV}) & & & & & & & \\ (\mathbf{IV}) & & & & & & & \\ (\mathbf{V}) & & & & & & & \\ (\mathbf{VI}) & & & & & & & \\ (\mathbf{VI}) & & & & & & & \\ \end{array}$$

acids corresponds to the H-O stretching mode of hydroxy-groups which are not hydrogen-bonded. In view of the resistance of the diboronic acids to aerial oxidation, the oxygen atom in such a hydroxy-group may form a weak dative bond to boron as in structure (X), so inhibiting the reaction of the latter with molecular oxygen.

Of the aromatic diboronic acids [II—VII; Y = $B(OH)_2$ only the p-phenylene compound [II; Y = B(OH)₂] has been adequately described previously; 9,10 we have raised the yield to 61%. 4,4'-Biphenylylenediboronic acid [III]; $Y = B(OH)_2$] is insoluble in aqueous solvents and so, unlike the other diboronic acids, could not be crystallised. The corresponding bis-2,2-dimethyltrimethylene ester [III; Y = (VIII)] was readily



purified however and the pure¹¹ diboronic acid was regenerated from this. The aminodiboronic acid [VI; $Y = B(OH)_2$ could not be obtained pure because of its

⁷ J. Goubeau and D. Hummel, Z. phys. Chem. (Frankfurt), 1959, **20**, 15.

⁸ H. C. Mattraw, C. E. Erickson, and A. W. Laubengayer, J. Amer. Chem. Soc., 1956, **78**, 4901.

 O. C. Musgrave, Chem. and Ind., 1957, 1152.
 D. R. Nielsen and W. E. McEwen, J. Amer. Chem. Soc., 1957, 79, 3081.

¹¹ Cf. K. Kitasaki and G. W. Willcockson, U.S.P. 3,203,908/ 1965 (Chem. Abs., 1965, 63, 18,150h).

rapid decomposition in air and in aqueous solvents to boric acid and N-ethyldiphenylamine, but the corresponding bis-2,2-dimethyltrimethylene ester [VI; Y =(VIII)] was stable. Whereas phenylboronic acid shows a single i.r. hydroxy-band at 3235 cm.⁻¹, all these diboronic acids have two hydroxy-stretching frequencies but these appear as well resolved doublets in the spectra of only the p-phenylene derivative (at 3260 and 3390 cm.⁻¹) and the 4,4'-biphenylylene derivative (at 3300 and 3390 cm.⁻¹). p-Phenylenediboronic acid [II; $Y = B(OH)_2$] reacts with pentaerythritol in boiling water to form the polymeric ester (XI). When this same acid was heated with butanol the yields of the resulting tetrabutyl ester [II; $Y = B(OBu)_{2}$] were variable, depending partly on the time taken for the distillation of the product. Specimens of the pure ester which had been heated for several hours under nitrogen at 210° contained tributyl borate, showing that some disproportionation ¹² of the diboronate occurs under these conditions. The hydrogenolysis of thiophen-2,5-dividiboronic acid [VII; $Y = B(OH)_{2}$] by Raney nickel¹³ provided an alternative synthesis of tetramethylenediboronic acid [I; n = 4, $Y = B(OH)_2$].

The aromatic diboronic acids lose water when heated in vacuo at temperatures above 230°, and the resulting polymeric anhydrides do not melt below 400°. The latter are more resistant to thermal degradation than are the polymethylenediboronic anhydrides. Thus p-phenylenediboronic anhydride, (p-OB·C₆H₄·BO)_n, was unaffected when heated at 450° in vacuo,⁹ whereas tetramethylenediboronic anhydride, (OB·[CH2]4·BO)n, underwent complete pyrolysis under these conditions. The volatile products included methane, ethylene, but-1-ene, and cis- and trans-but-2-ene, unidentified higher hydrocarbons, and organoboron compounds; the residue was a mixture of metaboric acid and diboron trioxide. 4,4'-Oxybisphenylboronic acid $[IV; Y = B(OH)_2]$, which was obtained as the monohydrate, is exceptionally resistant to dehydration and complete anhydride formation required prolonged heating in vacuo at 335°. The anhydride showed some i.r. hydroxyabsorption, suggesting that deboronation had occurred with the formation of a little metaboric acid.

The diboronic acids [II and VII; $Y = B(OH)_{o}$] form 1:1 complexes with 4-dimethylaminopyridine which are not readily hydrolysed by water and do not have definite melting points. The bis-2,2-dimethyltrimethylene diboronates [I (n = 4), II, and VII; Y = (VIII) form 1:2 or 2:3 complexes which can be crystallised without decomposition.

Reagents which bring about the scission of the carbon-boron bonds 14 of monoboronic acids cause

¹² Cf. E. W. Abel, W. Gerrard, and M. F. Lappert, J. Chem. Soc., 1958, 1451. ¹³ H. Hauptmann and W. F. Walter, Chem. Rev., 1962, **62**,

^{347;} G. R. Pettit and E. E. van Tamelen, Org. Reactions, 1962,

^{12, 356.} ¹⁴ M. F. Lappert, in 'The Chemistry of Boron and its Compounds,' ed. E. L. Muetterties, Wiley, New York, 1967, p. 566.

similar deboronation reactions with the diboronic Thiophen-2,5-diyldiboronic acid [VII; Y =acids. B(OH)₂] is readily hydrolysed by boiling water to boric acid and thiophen (isolated as its bismercurichloride derivative). When this diboronic acid was heated at 275°/0·1 torr, dehydration was accompanied by some deboronation and loss of thiophen, and the product appeared to be a mixture of the corresponding dianhydride (0.75 mol.) and metaboric acid (0.25 mol.). 4,4'-Bibenzylylenediboronic acid $[V; Y = B(OH)_2]$ and p-phenylenediboronic acid [II; Y = B(OH)₂] are much more resistant to hydrolysis but when boiled with water for several days were partly converted into bibenzyl and phenylboronic acid respectively. Alkaline solutions of p-phenylenediboronic acid absorb oxygen at room temperature. The use of aqueous sodium hydroxide results in dark water-soluble products: 2,5-bismethylamino-1,4-benzoquinone can be isolated after a few days from a solution in aqueous methylamine. It seems likely that in both these reactions oxidation and deboronation initially give 1,4-benzoquinone, which then undergoes further changes. Under similar conditions 4,4'-biphenylylenediboronic acid [III; $Y = B(OH)_2$ is unaffected.

Alkylboronic acids, RB(OH)2, are deboronated by ammoniacal silver nitrate 6 with the formation usually of the hydrocarbon R-R. The treatment of tetramethylenediboronic acid [I; n = 4, $Y = B(OH)_2$] with silver nitrate in sodium hydroxide solution resulted in the immediate precipitation of silver and the formation of ethylene (3.8%) and but-1-ene (3.5%) together with an intractable mixture of higher hydrocarbons and other compounds. The more volatile products are those which would result from the initial formation of tetramethylenedisilver and its subsequent decomposition to the tetramethylene biradical. Aromatic boronic acids ArB(OH)₂ react with silver nitrate in neutral or ammoniacal solution to form insoluble yellow silver derivatives which give the corresponding hydrocarbons ArH in good yields when heated in water.^{15,16} When *p*-phenylenediboronic acid [II; $Y = B(OH)_2$] was heated with silver nitrate in sodium hydroxide solution, benzene (95%) was obtained as expected. The intermediate yellow silver compound appeared to be stable in the reaction mixture at 0° but when dry exploded on being warmed above 50°. Because so little is known about the composition of such silver compounds ¹⁵ we examined further the more stable product obtained in a similar manner from phenylboronic acid. The analytical data for this substance are in agreement with the formula $C_{12}H_{10}Ag_4B_4O_7$, and its ready decomposition in boiling water to give benzene (91%), and in boiling benzene to give biphenyl, indicate that it is a complex

of phenylsilver. We consider that it is analogous to the complex 2C₆H₅Ag,AgNO₃ which has previously been described,^{17,18} and is best formulated as 2C₆H₅Ag,Ag₂- B_4O_7 . The unstable silver derivative obtained from p-phenylenediboronic acid appears from its reactions and from its silver content to be a complex of p-phenylenedisilver having the related formula C₆H₄Ag₂,Ag₂B₄O₇.

Part of this work is the subject of patents 19,20 and has been referred to briefly elsewhere.²¹

EXPERIMENTAL

M.p.s were determined for compounds in Pyrex capillaries evacuated to 0.1 torr. The identities of products were established by (a) comparison of i.r. spectra (recorded for Nujol mulls, liquid films, or gases with Perkin-Elmer Infracord model 137 or Hilger H800 spectrophotometers) with those of authentic specimens and, where appropriate, (b) mixed m.p. determinations. Nitrogen was determined by the Kjeldahl method, and boron by photometric titration (Thymol Phthalein) in aqueous ethanol with 0.1Msodium hydroxide in the presence of a large excess of mannitol. The boron contents of the aliphatic diboronic acids were also determined by similar photometric titrations (Bromothymol Blue) of the boric acid formed by their oxidation with alkaline hydrogen peroxide.^{6,8}

Difunctional Grignard Reagents: Preparation and Reactions with Trimethyl Borate .- A solution of the appropriate dihalide (1 mol.) in tetrahydrofuran (peroxide-free; distilled from sodium) was added slowly with stirring to a mixture of magnesium turnings (2 mol.) and dry tetrahydrofuran under dry nitrogen. The reaction was initiated by the addition of iodine or of a reacting mixture of magnesium, 1,2-dibromoethane, and tetrahydrofuran. The resulting mixture was heated under reflux for 3-20 hr. depending on the reactivity of the dihalide used. The use of magnesium activated by being heated with iodine appeared to promote the more sluggish reactions. Several of the resulting bifunctional Grignard reagents were poorly soluble in tetrahydrofuran but were handled without difficulty as suspensions. In each case the reagent was added dropwise under dry nitrogen to a vigorously stirred solution of freshly distilled trimethyl borate in dry ether, the temperature of the mixture being kept below -70° .

Bis-2,2-dimethyltrimethylene Diboronates .- A mixture of the diboronic acid (0.01 mole) and 2,2-dimethylpropane-1,3-diol (0.02 mole) was heated under reflux in dry benzene (100 ml.) under a Dean-Stark head. After the completion of the reaction, evaporation of the benzene gave the which was unaffected by atmospheric diboronate, moisture.22

Aliphatic Diboronic Acids.—(a) Tetramethylenediboronic acid. The Grignard reagent prepared from 1,4-dichlorobutane (127.0 g.) and magnesium turnings (52.0 g.) in tetrahydrofuran (900 ml.) was added while still warm to a solution of trimethyl borate (208 g.) in dry ether (1400 ml.) at -70° . After being stirred overnight at room temperature the mixture was added with stirring to a mixture

¹⁵ A. Michaelis and P. Becker, Ber., 1882, **15**, 180.

¹⁶ A. Michaelis and M. Behrens, Ber., 1894, 27, 244.

E. Krause and M. Schmitz, Ber., 1919, 52B, 2150.
 F. Challenger and O. V. Richards, J. Chem. Soc., 1934, 405.
 H. R. Goldschmid, B.P. 864,473/1961 (Chem. Abs., 1961, 55, 1964). 20,960g).

²⁰ O. C. Musgrave and H. R. Goldschmid, B.P. 895,917/1962 (Chem. Abs., 1962, 57, 6136f).

²¹ W. R. Bamford and S. Fordham, in 'High Temperature Resistance and Thermal Degradation of Polymers,' Soc. Chem. Ind. Monograph no. 13, 1961, p. 320. ²² Cf. R. A. Bowie and O. C. Musgrave, J. Chem. Soc., 1963,

^{3945.}

of ice (1400 g.) and concentrated sulphuric acid (108 ml.). The solid (A) which separated at the interface of the two layers was collected and the aqueous layer was thoroughly extracted with ether. The combined extracts were evaporated at $60^{\circ}/20$ torr and the residual solid was thoroughly washed with ether (200 ml.) and combined with the solid (A) to give the crude diboronic acid (66.7 g.). Concentration of the aqueous layer to 600 ml. gave more acid (26.2 g.), which was less readily purified. Repeated crystallisation of the acid from water until its i.r. spectrum no longer showed the bands at 2280 and 882 cm.⁻¹ characteristic of boric acid ²³ gave tetramethylenediboronic acid (80.0 g., 55%) as needles which, when heated slowly at 0.1 torr sintered at ca. 130° and evolved water and which, on rapid heating, appeared to have m.p. 177-179° (lit.,⁵ 179-181°) [Found (after drying at 20°/0.1 torr over silica gel): B (by oxidation) 15.0; B (direct titration), 14.5; OH, 47.65. Calc. for C₄H₁₂B₂O₄: B, 14.85; 4 OH, 46.7%]. The hydroxy-group content was determined by titration in methanolic solution with Fischer's reagent.⁸ The acid was unaffected by prolonged storage in vacuo over phosphorus pentoxide.

(b) Others. The following were prepared in a similar manner from the corresponding dichloroalkanes: pentamethylenediboronic acid (38%) [Found: B (by oxidation), 13.5; B (direct titration), 13.3. Calc. for $C_5H_{14}B_2O_4$: B, 13.55%]; hexamethylenediboronic acid (53%) [Found: B (by oxidation), 12.2; B (direct titration), 12.4. Calc. for $C_6H_{16}B_2O_4$: B, 12.45%]. Decamethylenediboronic acid (57%) [Found: B (by oxidation), 9.45; B (direct titration), 9.25. $C_{10}H_{24}B_2O_4$ requires B, 9.4%] was prepared from 1,10-dibromodecane and crystallised from dioxan.

Oxidation of Decamethylenediboronic Acid.-Hydrogen peroxide solution (30%; 5 ml.) was added dropwise to a solution of the diboronic acid (0.1 g.) in 4M-sodium hydroxide on a steam-bath. The solid which separated crystallised from ethanol-benzene to give decane-1,10-diol, m.p. 71-72° (lit.,²⁴ 72.2°) (Found: C, 69.0; H, 12.4. Calc. for $C_{10}H_{22}O_2$: C, 68.9; H, 12.7%).

Derivatives of Tetramethylenediboronic Acid.-(a) When the acid was heated at $120-130^{\circ}/0.1$ torr to constant weight (2.5 hr.) [Found: H₂O evolved, 25.27. C₄H₁₂B₂O₄ \longrightarrow (C₄H₈B₂O₂)_n requires 2H₂O, 24.75%], tetramethylenediboronic dianhydride was obtained as a glass [Found: B (by oxidation), 19.5. $(C_4H_8B_2O_2)_n$ requires B, 19.7%]. The acid also underwent dehydration when heated under reflux for 2 hr. with toluene in a Dean-Stark apparatus, but the toluene was not completely removed by heating the product at $100^{\circ}/0.1$ torr for 2 hr. (Found: H₂O evolved, 24.25; B, 18.9%).

(b) Bis-2,2-dimethyltrimethylene tetramethylenediboronate crystallised from light petroleum (b.p. 40-60°) at low temperature as plates, m.p. 58.5-59.5° (Found: B, 8.0. $C_{14}H_{28}B_2O_4$ requires B, 7.7%).

(c) A mixture of the acid (1.43 g.), o-phenylenediamine (2.16 g.), and benzene (100 ml.) was heated under reflux for 18 hr. in a Dean-Stark apparatus. The solid which separated on cooling crystallised (charcoal) from chloroform giving 1,4-di-(1,3,2-benzodiazaborol-2-yl)butane as prisms, m.p. 242-245° (Found: N, 19.1. C₁₆H₂₀B₂N₄ requires N, 19.3%).

Bis-2,2'-iminodiethyl Polymethylenediboronates.---A mix-

23 D. E. Bethell and N. Sheppard, Trans. Faraday Soc., 1955, 51, 9. ²⁴ P. Chuit, *Helv. Chim. Acta*, 1926, 9, 264.

ture of tetramethylenediboronic acid (1.45 g.), bis-(2hydroxyethyl)amine (diethanolamine) (2.1 g.) and dry benzene (100 ml.) was heated under reflux for 24 hr. in a Dean-Stark apparatus. Evaporation of the solvent and crystallisation of the residue from methanol-acetone gave bis-2,2'-iminodiethyl tetramethylenediboronate (2.3 g.) as needles, m.p. 250.5-251.5° (lit., 5 254-255°, 246-247°) (Found: N, 9.8. Calc. for $C_{12}H_{26}B_2N_2O_4$: 9.85%). The following diboronates were prepared in a similar manner: pentamethylene-, m.p. 238.5-240.5° (lit., 5, 25 235-237°, 241-243°) (Found: N, 9.45. Calc. for C13H28- $B_2N_2O_4$: N, 9.4%); hexamethylene-, m.p. 255.5-256.5° (lit., ${}^{25}263-265^{\circ}$) (Found: N, 8.8. Calc. for $C_{14}H_{30}B_2N_2O_4$: N, 9.0%); decamethylene-, m.p. 216-218° (Found: N, 7.4. $C_{18}H_{38}B_2N_2O_4$ requires N, 7.6%).

Aromatic Diboronic Acids.—(a) p-Phenylenediboronic acid. The Grignard reagent prepared from p-dibromobenzene (236 g.), magnesium (50 g.), and tetrahydrofuran (1500 ml.) was added during 3 hr. to a solution of trimethyl borate (208 g.) in dry ether (400 ml.) at -70° . The mixture was stirred for 2 hr., kept for 2 days, diluted with ether (200 ml.) and added to a stirred mixture of crushed ice (2 kg.) and concentrated sulphuric acid (60 ml.). The addition of ether (200 ml.) and water (1.25 l.) facilitated the separation of the organic and the aqueous layers. The aqueous layer was extracted repeatedly with ether (4 \times 400 ml.) and the combined organic extracts were evaporated on a steam-bath, finally at $100^{\circ}/20$ torr. The resulting solid was crushed, extracted thoroughly with cold ether $(6 \times 500 \text{ ml. portions})$, and dried at 120° for 2 hr. The i.r. absorption of the residue showed that it was virtually pure p-phenylenediboronic acid (101.8 g., 61%). Crystallisation from water gave the pure acid (90.5 g., 54%) (Found: B, 13.1. Calc. for C₆H₈B₂O₄: B, 13.05%).

In a similar experiment in which the mixture was stirred for only 1.5 hr. before being hydrolysed a lower (42%)yield of crude *p*-phenylenediboronic acid was obtained.

Azeotropic esterification of the diboronic acid with o-hydroxybenzyl alcohol gave bis-o-benzylene p-phenylenediboronate as needles m.p. 178-179° [from chloroformlight petroleum (b.p. 80-90°)] (Found: C, 70.4; H, 4.9. $C_{20}H_{16}B_2O_4$ requires C, 70.2; H, 4.7%).

(b) Others. 4,4'-Biphenylylenediboronic acid. Prepared from 4,4'-dibromobiphenyl as described in (a), the crude product was extracted repeatedly with aqueous 2M-sodium hydroxide. The filtrate was acidified, and the resulting precipitate was washed successively with water, acetone, and ether, giving the crude diboronic acid (48.6 g., 50%) as a finely divided solid. This gave bis-2,2-dimethyltrimethylene 4,4'-biphenylylenediboronate which crystallised from light petroleum (b.p. 60-80°) as prisms (7.3 g.), m.p. $250-251^{\circ}$ [Found: B, $5\cdot8\%$; M (ebullioscopic in acetone), 409. C₂₂H₂₈B₂O₄ requires B, 5.7%; M, 378.1]. A solution of the pure diboronate in aqueous sodium hydroxide was extracted continuously with ether for 2 days under nitrogen to remove 2,2-dimethylpropane-1,3-diol. Acidification of the aqueous layer gave the diboronic acid as a finely divided solid (Found: B, 9.15. C12H12B2O4 requires B, 8.95%) which could not be crystallised from water or from organic solvents.

4,4'-Oxybisphenylboronic acid. Prepared from 4,4'-dibromodiphenyl ether as described in (a), the *diboronic*

²⁵ L. I. Zakharkin and A. I. Kovredov, Izvest. Akad. Nauk S.S.S.R., Otdel khim. Nauk, 1962, 1564 (Chem. Abs., 1963, 58, 9107e).

acid monohydrate (46%) crystallised from water (as plates) or aqueous acetone (as prisms) (Found: B, 7.85. C₁₂H₁₂-B₂O₅,H₂O requires B, 7.85%). Bis-2,2-dimethyltrimethylene 4,4'-oxybisphenylboronate separated in plates, m.p. 199-201°, from carbon tetrachloride-light petroleum (b.p. 80-90°) (Found: B, 5.6. C₂₂H₂₈B₂O₅ requires B, 5.5%). Dehydration of the diboronic acid monohydrate by heating at $335^{\circ}/0.05$ torr for 11 hr. gave the corresponding dianhydride as an involatile solid [Found: B, 9.85. $(C_{12}H_8B_2O_3)_n$ requires B, 9.75%].

4,4'-Bibenzylylenediboronic acid. Prepared from 4,4'-dibromodibenzyl²⁶ as described in (a), the diboronic acid (63%) crystallised from aqueous acetone in fine needles (Found: B, 7.85. C₁₄H₁₆B₂O₄ requires B, 8.0%). Bis-2,2-dimethyltrimethylene 4,4'-bibenzylylenediboronate separated as prisms, m.p. 239.5-240.5° from chloroformcarbon tetrachloride (Found: B, 5.2. C24H32B2O4 requires B, $5\cdot3\%$). When heated at $240^{\circ}/0.1$ torr to constant weight (1.5 hr.) [Found: H₂O evolved, 13.9. C₁₄H₁₆B₂O₄ \longrightarrow (C₁₄H₁₂B₂O₂)_n requires 2H₂O, 13.5%] the acid gave 4,4'-bibenzylylenediboronic dianhydride as a solid which did not melt below 400° [Found: B, 9.0. $(C_{14}H_{12}B_2O_2)_n$ requires B, 9.25%].

Bis-2,2-dimethyltrimethylene 4,4'-ethyliminobisphenylboronate. Prepared from 4,4'-dibromo-N-ethyldiphenylamine 27,28 as described in (a), the impure diboronic acid was obtained as a reactive grey-green solid. This gave bis-2, 2-dimethyltrimethylene 4, 4'-ethyliminobisphenylboronate which crystallised from carbon tetrachloride-light petroleum (b.p. 80-90°) (charcoal) as felted needles, m.p. $214-214\cdot 5^{\circ}$ (Found: B, 5·15; N, 3·0. $C_{24}H_{33}B_2NO_4$ requires B, 5.15; N, 3.3%).

Thiophen-2,5-diyldiboronic acid. Prepared from 2,5-dibromothiophen²⁹ as described in (a), the diboronic acid was obtained as needles (62%) by rapid crystallisation (charcoal) from water (Found: B, 12.65; S, 18.4. C₄H₆B₂-O₄S requires B, 12.6; S, 18.65%). Bis-2,2-dimethyltrimethylene thiophen-2,5-diyldiboronate separated as needles, m.p. 156.5—157.5°, from chloroform-light petroleum (b.p. 80–90°) (Found: B, 7·1; S, 10·2. $C_{14}H_{22}B_2O_4S$ requires B, 7.0; S, 10.4%), bis-o-phenylene thiophen-2,5-diyldiboronate as needles, m.p. 242.5-243.5°, from chloroformcarbon tetrachloride (Found: S, 10.1. C₁₆H₁₀B₂O₄S requires S, 10.0%), and bis-o-benzylene thiophen-2,5-diyldiboronate as needles, m.p. 205.5-206.5°, from chloroform (Found: S, 9.3. $C_{18}H_{14}B_2O_4S$ requires S, 9.2%). When heated for 5 hr. at $275^{\circ}/0.1$ torr the diboronic acid gave a mixture of the corresponding anhydride (0.75 mol.) and metaboric acid (0.25 mol.) as a solid which did not melt below 400° [Found: S, 21.3. Calc. for $3(C_4H_2B_2O_3S)_n$ + (HBO₂)_n: S, 21.3%].

Bis-2,2'-iminodiethyl Arylenediboronates.-The addition of a hot solution in acetone of bis-(2-hydroxyethyl)amine (2 mol.) to a solution of the aromatic diboronic acid (1 mol.) in the same solvent gave a precipitate of the corresponding ester, which then crystallised in needles (83-88%) from aqueous acetone or from dimethylformamide-acetone. The following bis-2,2'-iminodiethyl esters were prepared in this manner: p-phenylenediboronate, m.p. 292-294° (decomp.) (Found: C, 55·1; H, 7·5; N, 9·4. C₁₄H₂₂B₂N₂O₄

²⁶ R. E. Buckles and N. G. Wheeler, Org. Synth., 1963, Coll. vol. 4, p. 256.

A. Skita, F. Keil, and H. Havemann, Ber., 1933, 66, 1400. 28 J. Forrest, D. A. Liddell, and S. H. Tucker, J. Chem. Soc., 1946, 454.

requires C, 55.3; H, 7.3; N, 9.2%); thiophen-2,5-diyldiboronate, m.p. 247-249° (decomp.) (Found: N, 9.3; S, 10.2. C₁₂H₂₀B₂N₂O₄S requires N, 9.05; S, 10.35%); 4,4'biphenylylenediboronate, m.p. 277-278° (decomp.) (Found: N, 7.8. C₂₀H₂₆B₂N₂O₄ requires N, 7.4%); 4,4'-bibenzylylenediboronate, m.p. 269-272° (Found: N, 7.1. C22H30B2- $\rm N_2O_4$ requires N, 6.85%).

Pentaerythritol p-Phenylenediboronate.-A solution of pentaerythritol (1.36 g.) in boiling water (20 ml.) was added to a boiling solution of p-phenylenediboronic acid (1.66 g.) in water (80 ml.) and the mixture was boiled for 5 min. Filtration gave the polymeric ester as a powder $(2\cdot 3 \text{ g}.)$ which was insoluble in water and in organic solvents [Found: B (by solution in an excess of aqueous sodium hydroxide and back-titration), 9.15. $(C_{11}H_{12}B_2O_4)_n$ requires B, 9.4%].

Thermal Disproportionation of Tetrabutyl p-Phenylenediboronate.---A mixture of butanol (100 ml.) and p-phenylenediboronic acid (10 g.) was distilled slowly until all the water-butanol azeotrope (b.p. 92-94°) had been removed. Distillation under reduced pressure gave tetrabutyl p-phenylenediboronate (18·8 g.), b.p. 170—172°/0·3 torr (lit.,^{10,30} b.p. 152—162°/0·1 torr; 160—176°/0·4 torr). The latter was heated under dry nitrogen for 4 hr. at 200-210°. Distillation then gave the unchanged ester (15.2 g.), b.p. 180°/0.4 torr, together with some tributyl borate (1.3 g.) b.p. 80°/0.4 torr.

Complexes of Diboronic Acids with 4-Dimethylaminopyridine.—A solution of 4-dimethylaminopyridine (1.0 g.)in methanol (10 ml.) was added to a solution of p-phenylenediboronic acid (0.5 g.) in the same solvent (10 ml.). The 1:1 complex (0.9 g.) which separated on cooling crystallised from methanol-acetone in prisms (Found: N, 9.4. $C_{13}H_{18}B_2N_2O_4$ requires N, 9.7%). A similar reaction with thiophen-2,5-diyldiboronic acid gave the corresponding 1:1 complex (Found: N, 9.9; S, 10.9. $C_{11}H_{16}B_2N_2O_4S$ requires N, 9.55; S, 10.9%).

Complexes of Bis-2,2-dimethyltrimethylene Diboronates with 4-Dimethylaminopyridine.--A solution of the tetramethylenediboronate (0.7 g.) in acetone (10 ml.) was added to a solution of 4-dimethylaminopyridine (2.0 g.) in the same solvent (10 ml.). The 1:2 complex separated as prisms (0.95 g.), m.p. 93-95° (Found: C, 63.7; H, 8.7; N, 10.9. $C_{14}H_{28}B_2O_4, 2C_7H_{10}N_2$ requires C, 63.9; H, 9.2; N, 10.65%). A similar reaction with the thiophen-2,5-divldiboronate gave the corresponding 1:2 complex as plates from acetone, m.p. 151-152° (Found: C, 60.6; H, 7.8; N, 9.8; S, 6.1. C₁₄H₂₂B₂O₄S, 2C₇H₁₀N₂ requires C, 60.9; H, 7.65; N, 10.15; S, 5.8%). The reaction with the p-phenylenediboronate (in chloroform) gave the corresponding 2:3 complex as needles, m.p. 136-138° (Found: N, 8.75. $2C_{16}H_{24}B_2O_4, 3C_7H_{10}N_2$ requires N, 8.65%).

Hydrogenolysis of Thiophen-2,5-diyldiboronic Acid.-A mixture of the diboronic acid (1.72 g.), methanol (150 ml.), and freshly prepared Raney nickel W-2³¹ (ca. 20 g.) was heated under reflux with stirring for 3 hr. and filtered. The filtrate was diluted with water (20 ml.) and evaporated under reduced pressure to give tetramethylenediboronic acid (0.2 g., 14%) which with bis-(2-hydroxyethyl)amine

²⁹ R. Mozingo, S. A. Harris, D. E. Wolf, C. E. Hoffhine, N. R.

Easton, and K. Folkers, *J. Amer. Chem. Soc.*, 1945, 67, 2092. ³⁰ J. E. Mulvaney, J. J. Bloomfield, and C. S. Marvel, *J. Polymer Sci.*, 1962, 62, 59.

³¹ R. Mozingo, Org. Synth., 1955, Coll. vol. 3, p. 181.

formed bis-2,2'-iminodiethyl tetramethylenediboronate, m.p. 249-251°.

Hydrolytic Deboronation of Arylenediboronic Acids.— (a) p-Phenylenediboronic acid (8.3 g.) was boiled with water (250 ml.) for 4 days under reflux, then cooled, and the unchanged acid (7.0 g., 84%) which crystallised was collected. Extraction of the filtrate with ether gave a mixture (0.3 g.) of approximately equal amounts (i.r. spectrum) of phenylboronic anhydride and p-phenylenediboronic acid. Extraction of this with boiling toluene and concentration of the resulting solution gave phenylboronic anhydride (50 mg.).

(b) Thiophen-2,5-diyldiboronic acid (2 g.) was boiled with water (100 ml.) for 5 hr. and the solution was distilled with steam. The distillate, which did not contain boronic acids (titration with alkali), was shaken with mercury(II) chloride (5.5 g.) and sodium acetate (10 g.) for 2 hr. and kept for 3 days, giving thiophen-2,5-diyldimercury(II) dichloride $(2\cdot3 g., 36\%)$ as a voluminous precipitate.

(c) 4,4'-Bibenzylylenediboronic acid (0.96 g.) was boiled with water (50 ml.) for 3 days; the mixture was then made alkaline and extracted with ether. Evaporation of the ethereal layer and crystallisation of the residue (0.1 g.; m.p. 45-47°) from ethanol gave bibenzyl. Acidification of the alkaline solution gave unchanged diboronic acid (0.58 g., 60.5%).

Oxidation of p-Phenylenediboronic Acid in Alkaline Solution.—(a) A solution of the diboronic acid (5 g.) in M-sodium hydroxide was shaken under oxygen for 40 hr. Considerable absorption of oxygen occurred and acidification of the dark solution gave unchanged diboronic acid (1.7 g., 34%) as the only identifiable product.

(b) A mixture of the diboronic acid (0.1 g.) and ethanolic methylamine (33% w/w; 10 ml.) remained colourless after being kept under oxygen for 3 days. The addition of water (1 ml.) caused the solution to become purple and after 7 days 2,5-bismethylamino-1,4-benzoquinone had separated as red needles (from ethanol), m.p. 282-285° (decomp.) [lit.,³² 284-286° (decomp.)].

Reaction of Phenylboronic Anhydride with Alkaline Silver Nitrate.—(a) A solution of silver nitrate (8.5 g.) in water (50 ml.) was added dropwise with stirring at 0° to a solution of phenylboronic anhydride (5.2 g.) and sodium hydroxide (2 g.) in water (150 ml.). The precipitate was washed with ice-water until the washings were free from silver ions, then with ethanol, and dried at 0°/0.02 torr giving bi[phenylsilver(I)]-disilver(I) tetraborate as a yellow powder (Found: C, 19.5; H, 1.5; Ag, 59.5. C₁₂H₁₀- $Ag_2, Ag_2B_4O_7$ requires C, 19.45; H, 1.35; Ag, 58.25%). For the determination of the silver content a sample was heated first with water and then with dilute nitric acid until the solid had dissolved, and the resulting solution was titrated with ammonium thiocyanate.

The phenylsilver complex (3.0 g.) was heated under reflux with benzene (100 ml.) for 1 hr. Filtration gave a black residue (Found: Ag, 74.6. Calc. for $2Ag + Ag_2B_4O_7$: Ag, 73.55%). Evaporation of the filtrate and sublimation of the oily residue at 90°/20 torr yielded biphenyl as plates, m.p. 66—68°.

(b) A solution of silver nitrate (17 g.) in water (100 ml.) was added to a solution of phenylboronic anhydride (10.4 g.) and sodium hydroxide (5 g.) in water (200 ml.). Next day the mixture was heated under reflux in a 'heavy entrainer' Dean-Stark apparatus; benzene (7.9 ml., 91%) was obtained.

Reactions of Diboronic Acids with Alkaline Silver Nitrate.— (a) A solution of silver nitrate (68 g.) in water (300 ml.) was added dropwise during 30 min. to a stirred solution of tetramethylenediboronic acid (29·2 g.) and sodium hydroxide (22 g.) in water (400 ml.) over which nitrogen was passed. The mixture of volatile products which condensed at -196° separated when warmed to $-120^{\circ}/$ 0·1 torr into (gaseous) ethylene (0·42 g., 3·8%) and (liquid) but-1-ene (0·39 g., 3·5%).

(b) An aqueous solution of p-phenylenediboronic acid (8·3 g.) and sodium hydroxide (4 g.) was added with stirring to an aqueous solution of silver nitrate (17 g.) and the resulting yellow precipitate of p-phenylenedisilver(I)-disilver(I) tetraborate which darkened on exposure to light was washed with ice-water and with ethanol. When dry the product decomposed rapidly at room temperature and exploded at 50° (Found: Ag, 62·2. Calc. for C₆H₄Ag₂,Ag₂B₄O₇: Ag, 65·1%). Consistent analytical values could not be obtained.

(c) A solution of silver nitrate $(11\cdot3 \text{ g.})$ in water (100 ml.) was added with swirling to a solution of *p*-phenylenediboronic acid (5.5 g.) and sodium hydroxide (3.3 g.) in water (50 ml.). The mixture was heated under reflux in a 'heavy entrainer' Dean-Stark apparatus; benzene (2.85 ml., 95%) was obtained.

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32 W. K. Anslow and H. Raistrick, J. Chem. Soc., 1939, 1446.