418. *Polycondensations and Certain Other Reactions of Arylboron Chlorides.*

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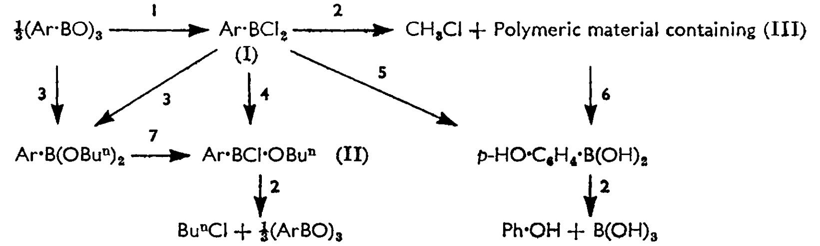
Experiments with derivatives of *p*-methoxyphenylboronic acid, phenylboron dichloride, and diphenylboron chloride are described. Two polycondensates have been isolated, which are thermally but not hydrolytically stable. *p*-Hydroxyphenylboronic acid was synthesised from *p*-methoxyphenylboron dichloride.

In the search for thermally and hydrolytically stable semi-inorganic polymers, we have investigated the potentialities of the new compounds *p*-methoxyphenylboron dichloride (I; Ar = *p*-MeO·C_6H_4), *n*-butyl *p*-methoxyphenylchloroboronite (II; Ar = *p*-MeO·C_6H_4), phenylboron dichloride, and diphenylboron chloride.

The experiments in the *p*-methoxyphenylboron series are illustrated by the annexed diagram (Ar = *p*-MeO·C_6H_4); *p*-methoxyphenylboronic anhydride had previously[1] been prepared.



Reagents: 1, BCl_3. 2, Heat. 3, $2Bu^nOH$. 4, Bu^nOH. 5, (*a*) BCl_3, heat; (*b*) H_2O. 6, H_2O (dearylation also occurred giving phenol and boric acid). 7, $ArBCl_2$.

The pyrolysis of *p*-methoxyphenylboron dichloride (I) was expected to produce the polymeric product (III) with elimination of methyl chloride because it has been shown[2] that phenylboron dichloride cleaves ethers, including aralkyl ethers according to: $Ar'OR + PhBCl_2 \longrightarrow Ph{\cdot}BCl{\cdot}OAr' + RCl$. Prolonged heating of *p*-methoxyphenylboron dichloride at 290—300° in fact afforded methyl chloride (100%), a solid, chlorine-containing polymeric material, and hydrogen chloride. The formation of hydrogen chloride can be accounted for by assuming that it arose from a Friedel–Crafts reaction resulting in cross-linking between polymer chains involving attachment of boron atoms from one chain to benzene nuclei of a neighbouring chain. Such a reaction would not be remarkable in view of the high temperature used and because the *p*-methoxyphenylboron dichloride or its polycondensate could act as the electron-deficient catalyst required for a Friedel–Crafts reaction.

$MeO{\cdot}[C_6H_4{\cdot}BCl{-}O]_n{\cdot}C_6H_4{\cdot}BCl_2$ (III)

$Ph{-}[BCl{\cdot}C_6H_4{\cdot}]_m{\cdot}BClPh$ (IV)

The polymeric material was readily hydrolysed and the identity of the principal product as *p*-hydroxyphenylboronic acid was established by comparing its characteristics, particularly infrared spectrum, with those of a sample synthesised independently. The presence of boric acid and phenol in the hydrolysis product is accounted for by assuming dearylation during polymerisation; it was also shown that heating *p*-hydroxyphenylboronic acid gave the same products (for similar dearylations see ref. 3).

p-Hydroxyphenylboronic acid, which was unknown at this time, was prepared from

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[1] Kuivila and Williams, *J. Amer. Chem. Soc.*, 1954, **76**, 2679; see also König and Scharrnbeck, *J. prakt. Chem.*, 1930, **128**, 157; Bean and Johnson, *J. Amer. Chem. Soc.*, 1932, **54**, 4415.

[2] Dandegaonker, Gerrard, and Lappert, *J.*, 1957, 2893.

[3] Abel, Gerrard, and Lappert, *J.*, 1957, 5051; 1958, 1451.

p-methoxyphenylboron dichloride, as shown in the reaction diagram, and this provides an interesting new use of boron trichloride. The acid has since been obtained by another route.[4]

Pyrolysis of *n*-butyl *p*-methoxyphenylchloroboronite (II) did not result in fission of the methoxy-group, but in slow formation of *p*-methoxyphenylboronic anhydride (see ref. 5 for similar reactions of alkyl phenylchloroboronites).

Diphenylboron chloride was stable at 200—210° (and even at 320°), but in the presence of aluminium chloride benzene equivalent to one group per mol was eliminated. No hydrogen chloride was liberated, as expected from a Friedel–Crafts condensation, and an infusible residue, which may have contained the polymeric material (IV), was obtained.

Phenylboron dichloride, when similarly heated in presence of aluminium chloride was much more stable.

EXPERIMENTAL

Analytical methods have been described previously.[5] Infrared spectral measurements were determined in a Grubb-Parsons S.3A double-beam model with a sodium chloride prism; samples were studied as capillary films or as solid mulls in paraffin oil.

Derivatives of p-*Methoxyphenylboronic Acid.*—*p*-Methoxyphenylboronic acid (26·5 g., 28%) was obtained by a standard procedure from *p*-methoxyphenylmagnesium bromide and tri-*n*-butyl borate (144 g.), and at 110—115° (10 hr.) afforded the anhydride (100%), m. p. 206—207° (Found: B, 8·0. Calc. for $C_7H_7O_2B$: B, 8·0%).

Boron trichloride (15·3 g.) at −39° was added to *p*-methoxyphenylboronic anhydride (17·1 g.) in methylene dichloride–chloroform (1 : 1) (200 c.c) at −80°, and the mixture was stored at −80° for 18 hr. Volatile matter was removed under reduced pressure, and from the residue, p-*methoxyphenylboron dichloride* (68%), m. p. 34—37°, b. p. 85°/0·05 mm. (Found: Cl, 36·8; B, 5·6. $C_7H_7OCl_2B$ requires Cl, 37·5; B, 5·7%), was extracted by 4 : 1 *n*-pentane–methylene dichloride.

By interaction with butan-1-ol (0·90 g.) in methylene dichloride (15 c.c.) at −10°, *p*-methoxyphenylboron dichloride (1·15 g.) afforded *di*-n-*butyl* p-*methoxyphenylboronate* (0·72 g.), b. p. 110—113°/0·3 mm., n_D^{22} 1·4825 (Found: B, 4·0. $C_{15}H_{25}O_3B$ requires B, 4·0%), identical (including infrared spectrum) with the compound obtained (81%), b. p. 105—106°/0·02 mm., n_D^{22} 1·4835 (Found: B, 4·1%), by azeotropic separation of water from a mixture of the anhydride, butan-1-ol, and benzene.

p-Methoxyphenylboron dichloride (9·7 g.) was heated at 225—250° for 50 hr. Methyl chloride (2·1 g., 81%) (Found: Cl, 69·7. Calc. for CH_3Cl: Cl, 70·3%) was condensed at −80°, and hydrogen chloride (1·0 g.) was received in a tube containing pellets of potassium hydroxide. The residue was a glass (5·82 g.) {Found: Cl, 5·8; B, 7·9. Calc. for $[C_6H_4B(Cl)O]_n$: Cl, 25·6; B, 7·8; and for $[C_6H_3B(O)]_m$: B, 10·5%}, which was insoluble in a wide range of organic solvents. The chlorine content of residues obtained in different experiments varied somewhat: *e.g.*, the dichloride (19·33 g.) heated at 290—300° for 70 hr. afforded methyl chloride (5·2 g., 100%), hydrogen chloride (0·64 g.), and a residue (Found: Cl, 14·5; B, 8·8%). In every experiment the Pyrex vessel suffered network fracture beneath the glassy solid, and this was not due to mere thermal treatment of the vessel.

The residues were easily hydrolysed. One residue (4·2 g.) (Found: Cl, 9·3; B, 6·9%) was shaken with water, and the ether-soluble matter, when freed from ether, comprised phenol (0·6 g.) [extracted by *n*-pentane and methylene dichloride (4 : 1)], m. p. 39—40°, b. p. 46—47°/0·1 mm. (trinitro-derivative, m. p. 118—119°) (identified also by its infrared spectrum), and *p*-hydroxyphenylboronic acid (2·45 g.) (Found: B, 7·5. Calc. for $C_6H_7O_3B$: B, 7·8%), m. p. 225—228° unchanged on addition of the specimen obtained as shown below, and having identical infrared spectra. Evaporation of the primary aqueous solution gave boric acid (0·28 g.).

n-*Butyl* p-*methoxyphenylchloroboronite* (1·70 g., 75%), b. p. 83—84°/0·02 mm., n_D^{18} 1·5020 (Found: Cl, 15·8; B, 4·8. $C_{11}H_{16}O_2ClB$ requires Cl, 15·7; B, 4·8%), and hydrogen chloride (0·38 g., 100%) were obtained from *p*-methoxyphenylboron dichloride (1·90 g., 1 mol.) and butan-1-ol (0·76 g., 1 mol.) in methylene dichloride (20 c.c.), which had been mixed at −80°.

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[4] Gilman, Santucci, Swayampati, and Ranck, *J. Amer. Chem. Soc.*, 1957, **79**, 3077.

[5] Dandegaonker, Gerrard, and Lappert, *J.*, 1957, 2872.

The same chloro-ester (1·70 g., 77%), b. p. 85—86°/0·02 mm., n_D^{18} 1·5018, d_4^{20} 1·036 (Found: Cl, 15·5; B, 4·7%), was obtained by mixing the dichloride (0·95 g.) and the dibutyl ester (1·27 g.) at 20°, followed by distillation.

After *n*-butyl *p*-methoxyphenylchloroboronite (2·36 g.) had been heated at 200—220° for 40 hr., part of it (0·80 g., 34%) was recovered (b. p. 84—86°/0·02 mm.) (Found: C., 15·5; B, 4·8%). *p*-Methoxyphenylboronic anhydride (0·90 g.) remained as an involatile residue, and *n*-butyl chloride (0·32 g.) was condensed at −80°. Neither methyl chloride nor hydrogen chloride was detected.

p-*Hydroxyphenylboronic Acid.*—*p*-Methoxyphenylboron dichloride (5·92 g., 1 mol.) and boron trichloride (3·70 g., 1 mol.) were heated at 110—115° for 120 hr. in a sealed tube. After removal of volatile matter at 20°/10 mm., the minimum quantity of water required to dissolve the solid residue was added and the solution was extracted with ether. The ether extract was dried (Na_2SO_4) and freed from solvent at 20°/10 mm. to give *p*-hydroxyphenylboronic acid (4·00 g., 94%), m. p. 210—215° (m. p. 229—232°, after three recrystallisations from methylene dichloride) (Found: C, 51·3; H, 5·38; B, 7·7. Calc. for $C_6H_7O_3B$: C, 52·2; H, 5·10; B, 7·8%). The aqueous portion afforded boric acid (1·99 g., 99%) (Found: B, 17·3. Calc. for H_3O_3B: B, 17·4%) on concentration *in vacuo*. The yields are based on: $MeO{\cdot}C_6H_4{\cdot}BCl_2 + BCl_3 \longrightarrow Cl_2B{\cdot}O{\cdot}C_6H_4{\cdot}BCl_2 + CH_3Cl \xrightarrow{5H_2O} (HO)_3B + HO{\cdot}C_6H_4{\cdot}B(OH)_2$. There was no reaction between the trichloride and *p*-methoxyphenylboron dichloride at 20°.

p-Hydroxyphenylboronic acid (1·73 g.) was heated (80 hr.) with water (0·23 g.) in a sealed tube at 230—240°. The product was shaken with water and 4 : 1 *n*-pentane–ether. Boric acid (0·76 g., 98%) was isolated from the aqueous fraction, and phenol (0·98 g., 91%), b. p. 50—52°/0·2 mm., m. p. 39—40° (trinitro-derivative, m. p. 119°) (identified also by its infrared spectrum), from the organic layer.

Pyrolysis of the Phenylboron Chlorides.—Diphenylboron chloride [6] (5·68 g.) was heated with aluminium chloride (0·20 g.) in a sealed tube at 170—180° for 40 hr. Benzene (1·65 g.), b. p. 80°, n_D^{22} 1·500 (dinitro-derivative, m. p. 89°), was then withdrawn at 60°/11 mm. and condensed at −80°; the residue, except the catalyst, was dissolved in methylene dichloride, and on evaporation of the solvent the solid residue (3·40 g.) [Found: B, 8·7. Calc. for (IV); B, 8·8%] comprised a substance, insoluble in *n*-pentane (0·6 g.) (Found: B, 5·3%), not melting up to 300°, and a sticky gum, soluble in *n*-pentane. When the reaction temperature was 200—210° (80 hr.), benzene (equivalent to removal of one phenyl group) was obtained, and after separation from the catalyst, the final residue contained a substance soluble in water, and another soluble in chloroform; but neither melted up to 300°. When pure diphenylboron chloride was heated at 320° in a sealed tube for 44 hr. subsequent distillation led to 85% recovery of the starting material.

Phenylboron dichloride [6] and aluminium chloride (0·2 g.) were heated at 170—180° (40 hr.) in a sealed tube. The dichloride (4·52 g., 76%), b. p. 58°/11 mm., n_D^{20} 1·5440 (Found: Cl, 43·4; B, 6·7. Calc. for $C_6H_5Cl_2B$: Cl, 44·6; B, 6·9%), was recovered. The residue afforded a gum (extracted with *n*-pentane) and an infusible residue. Hydrogen chloride was not evolved. Similarly half the dichloride was recovered when the temperature was 200—220° and the heating time was 80 hr.

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[6] Abel, Dandegaonker, Gerrard, and Lappert, *J.*, 1956, 4697.