The Preparation and Properties of Triphenyl Borate and the Phenoxyboron Chlorides.

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Certain differences in properties of phenyl, as compared with alkyl, esters containing boron have been observed. Whereas trialkyl borates (except trimethyl borate) show little tendency to form complexes with tertiary bases, triphenyl borate forms 1 : 1 addition compounds with pyridine, quinoline, and monoethylamine; ability of triphenyl borate to co-ordinate with diethylamine, triethylamine, and tri-*n*-butylamine decreased in that order. Triphenyl borate and the phenoxyboron chlorides were obtained by interaction in appropriate proportions of boron trichloride with phenol. The phenoxyboron chlorides disproportionate reversibly, and form relatively stable co-ordination complexes with pyridine. Distillation of of *tert.*-butyl alcohol with triphenyl borate afforded *iso*butylene and di*iso*butylene. No interaction between boron trichloride and diphenyl ether was observed.

Triphenyl borate (Pictet and Geleznoff, *Ber.*, 1903, **36**, 2219; Michaelis and Hillringhaus, *Annalen*, 1901, **315**, 41; Wuyts and Duquesne, *Bull. Soc. chim. Belg.*, 1939, **48**, 77; Gerrard and Lappert, *J.*, 1952, 1486) has now been prepared (83%) more conveniently than hitherto by interaction of boric acid and excess of phenol, the water produced being removed as a phenol–water azeotrope. Scattergood, Miller, and Gammon (*J. Amer. Chem. Soc.*, 1945, **67**, 2150) prepared alkyl borates in a similar way.

Phenyl dichloroboronite $PhO{\cdot}BCl_2$ was obtained by the interaction of boron trichloride with both phenol (*a*) and triphenyl borate (*b*), but it disproportionated readily even at −15° into triphenyl borate and boron trichloride, involving the intermediate formation of the chloroboronate (*b*) :

$$PhOH + BCl_3 \longrightarrow PhO{\cdot}BCl_2 + HCl \quad . \; . \; . \; . \; . \; . \; . \; . \quad (a$$

$$2(PhO)_3B \underset{-BCl_3}{\overset{BCl_3}{\rightleftharpoons}} 3(PhO)_2BCl \underset{-3BCl_3}{\overset{3BCl_3}{\rightleftharpoons}} 6PhO{\cdot}BCl_2 \quad . \; . \; . \; . \; . \; . \; . \quad (b)$$

By similar procedures, *n*-, *iso*-, and *sec.*-butyl dichloroboronites have been isolated (Gerrard and Lappert, *J.*, 1951, 2545), but these in contrast underwent irreversible decomposition to alkyl chloride, boron trichloride, and boron trioxide.

Diphenyl chloroboronate, prepared by the interaction of boron trichloride (1 mol.) and triphenyl borate (2 mols.), was considerably more stable than the dichloroboronite. Prolonged heating ultimately caused disproportionation into boron trichloride and triphenyl borate, but distillation under reduced pressure afforded a small fraction consisting of a mixture of chloroboronate and dichloroboronite. In addition a very small amount of dichloroboronite was found. These results indicate that the dichloroboronite is formed as an intermediate step in the disproportionation of the chloroboronate:

$$2(PhO)_2BCl \rightleftharpoons (PhO)_3B + PhO{\cdot}BCl_2$$

$$2PhO{\cdot}BCl_2 \rightleftharpoons (PhO)_2BCl + BCl_3$$

Like *n*-butyl dichloroboronite (Lappert, *J.*, 1953, 667) the phenoxyboron chlorides form stable solid 1 : 1 adducts with pyridine.

From the amount of hydrogen chloride evolved when butyl dichloroboronite was mixed with phenol (*c*), it appeared certain that the mixed ester was formed. Distillation afforded tri-*n*-butyl and triphenyl borate, and the addition of pyridine even at −70° led to the

$$Bu^nO{\cdot}BCl_2 + 2PhOH \longrightarrow Bu^nO{\cdot}B(OPh)_2 + 2HCl \quad . \; . \; . \; . \; . \; . \quad (c)$$

isolation of tri-*n*-butyl borate and the pyridine–triphenyl borate complex (cf. Thomas, *J.*, 1946, 823, with reference to mixed alkyl borates).

In an attempt to obtain *tert.*-butyl borate, *tert.*-butyl alcohol (2 mols.) was heated with triphenyl borate (1 mol.), but *iso*butylene and di*iso*butylene were formed. With methyl alcohol (3 mols.) and triphenyl borate (1 mol.) alcoholysis (52% in 3 hours at 90°) took place.

No reaction between boron trichloride and diphenyl ether occurred below 25°, whereas with methyl phenyl or ethyl phenyl ether boron trichloride readily caused fission of the (alkyl) C–O bond, forming alkyl chloride and phenyl dichloroboronite (Gerrard and Lappert, *J.*, 1952, 1486, *loc. cit.*). The first step postulated for the fission mechanism was the formation of a co-ordinate B–O link, but with diphenyl ether the nucleophilic character of the oxygen atom is apparently considerably reduced owing to the conjugation of the lone pairs of electrons on the oxygen atom with the phenyl groups. Similarly, diphenyl ether does not form a complex with boron trifluoride (Bowlus and Nieuwland, *J. Amer. Chem. Soc.*, 1931, **53**, 3835; Meerwein and Maier-Hüser, *J. pr. Chem.*, 1932, **134**, 51; Dornte, U.S.P., 2,559,062/1951), by contrast with other ethers.

Co-ordination of Borates with Amines.—Until recently, trialkyl borates were thought to be incapable of forming co-ordination compounds (see, *e.g.*, Sidgwick, " Chemical Elements and their Compounds," Oxford Univ. Press, London, 1950, p. 403). This has since been shown to be substantially correct except for the trimethyl homologue (Goubeau and Link, *Z. anorg. Chem.*, 1951, **267**, 27; Venkataramaraj Urs and Gould, *J. Amer. Chem. Soc.*, 1952, **74**, 2948).

Triphenyl borate forms co-ordination compounds more readily than trialkyl borates, because in the former the $+M$ effect from the oxygen to the aromatic nucleus, assisted by the $-I$ effect of the nucleus, leads to a lower electron density at the boron atom, whereas in the alkyl borates there can be back co-ordination from oxygen to boron (Lewis and Smyth, *J. Amer. Chem. Soc.*, 1940, **62**, 1529).

That the order of nucleophilic strength of the amines which co-ordinate with triphenyl borate is not the same as is found with hydrogen acids, for which $Et_2NH > Et{\cdot}NH_2 > Et_3N >$ pyridine, is probably explained in terms of steric effects (the *F*-strain theory of H. C. Brown *et al.*, *J. Amer. Chem. Soc.*, 1942, **64**, 32, and many subsequent papers) rather than of polar effects.

EXPERIMENTAL

General Procedures.—Methylene dichloride was used as a solvent because of its high volatility and good solvent properties. Hydrocarbon solvents were less effective, and diethyl ether was avoided in view of its reactivity with boron trichloride.

Analysis for boron in the presence of phenol was carried out by Thomas's method (*J.*, 1946, 820), conversion into trimethyl borate and hydrolysis of the latter to boric acid, estimated acidimetrically in presence of mannitol. The phenoxy-group was estimated by hydrolysis to phenol and iodometric estimation by conversion into the tribromo-derivative. Chlorine was estimated by the Volhard method, and amines in amine complexes by steam-distillation with alkali and titration of the distillate with sulphuric acid to bromophenol-blue.

Preparation and Reactions of Triphenyl Borate.—Triphenyl borate (291 g., 83%), b. p. 157—

158°/0·05 mm., 177—178°/0·5 mm., m. p. 92—93° (Found: B, 3·74; PhO, 96·5. Calc. for $C_{18}H_{15}O_3B$: B, 3·7; PhO, 96·3%), was prepared by heating phenol (560 g., 5·3 mols.) and boric acid (75 g., 1 mol.) at a temperature required for the distillation (through a column) of the 9 : 1 water–phenol azeotrope, b. p. 98—99°. The remaining phenol was removed at low pressure, and the borate was purified by distillation through a lagged and heated column, and by recrystallisation from methylene dichloride.

Hydrolysis. Water (0·55 g., 3 mols.) was added to the borate (2·037 g., 1 mol.) in methylene dichloride (5 ml.) and pentane (10 ml.), and the mixture was heated at 40° for 30 min. The boric acid was filtered off and washed free from phenol by pentane (Found: H_3BO_3, 0·435 g. Calc.: H_3BO_3, 0·435 g.). Evaporation of the solvent afforded a residue of phenol (1·96 g. Calc., 1·97 g.), b. p. 100°/45 mm.

Complexes. Pyridine (6·6 g., 1·1 mols.) was added slowly with shaking to a solution of the borate (20·2 g., 1 mol.) in methylene dichloride (10 ml.) and pentane (20 ml.), and the white precipitate of *pyridine complex* (26·8 g., 100%) (Found: B, 3·02; PhO, 75·3; C_5H_5N, 21·3. $C_{23}H_{20}O_3NB$ requires B, 2·93; PhO, 75·6; C_5H_5N, 21·4%) was filtered off and washed with pentane. The m. p. (148°) was not sharp, because decomposition occurs to the extent of 4% at 120° (0·5 hr.) and 12% at 150° (0·5 hr.). In moist air hydrolysis is complete in 5 days.

Quinoline (3·50 g., 1 mol.) in *n*-pentane (15 ml.) was added to triphenyl borate (7·88 g., 1 mol.) in methylene dichloride (15 ml.) at $-60°$. The *complex* (10·25 g., 90%) was precipitated at 20° and after being washed with pentane and kept at 2 mm. had m. p. 93—94° (Found: PhO, 65·5; C_9H_7N, 29·3; B, 2·74. $C_{27}H_{22}O_3NB$ requires PhO, 66·5; C_9H_7N, 30·8; B, 2·59%).

Dry ethylamine was passed into the borate (19·9 g., 1 mol.) in methylene dichloride (20 ml.) and pentane (30 ml.), and the white solid *complex* (23·0 g., 100%) was recrystallised from a mixture of the two solvents (Found: B, 3·17; PhO, 82·5; NH_2Et, 14·5. $C_{20}H_{22}O_3BN$ requires B, 3·23; PhO, 83·3; NH_2Et, 13·5%).

Attempts to prepare similarly the corresponding diethylamine complex led to a solid which was low in amine content (Found: B, 2·68; PhO, 80·5; $NHEt_2$, 17·6. Calc. for $C_{22}H_{26}O_3BN$: B, 2·99; PhO, 77·1; $NHEt_2$, 20·2%). Similarly with triethylamine or tri-*n*-butylamine the borate was precipitated and contained only 3—4% of amine. From the pentane washings the greater part of the pure amine was recovered. Similarly also, no evidence of reaction between the borate and di-*n*-butyl sulphide, diethyl ether, dioxan, or tetrahydrofuran was obtained.

Interaction of Phenol with Boron Trichloride.—(*a*) To phenol (29·55 g., 3 mols.) in methylene dichloride (100 ml.) at $-80°$, boron trichloride (12·3 g., 1 mol.) in methylene dichloride (25 ml.) at $-80°$ was added slowly with shaking. The mixture was then allowed to attain room temperature slowly. The solvent and hydrogen chloride were removed under reduced pressure. The triphenyl borate (25·4 g., 84%) was distilled (b. p. 136—137°/0·1 mm.), and then recrystallised from methylene dichloride (Found: B, 3·82%).

(*b*) By a similar procedure, but with the trichloride (6·3 g., 1 mol.) and phenol (5·0 g., 1 mol.) mixed at $-50°$, hydrogen chloride (1·95 g., 100% based on: $PhOH + BCl_3 \longrightarrow PhO{\cdot}BCl_2 + HCl$) was obtained at 20° (30 min.), the gas being collected in a tube containing moist potassium hydroxide. On removal of volatile matter at 15°/15 mm. the residue appeared to be a mixture of chloro-esters and triphenyl borate (Found: PhO, 64·1; Cl, 29·2; B, 6·04. Calc. for $C_{12}H_{10}O_2ClB$: PhO, 80·2; Cl, 15·2; B, 4·64. Calc. for $C_6H_5OCl_2B$: PhO, 53·2; Cl, 40·6; B, 6·19%).

Attempted Isolation of Phenyl Dichloroboronite.—(*a*) Addition of triphenyl borate (3·43 g., 1 mol.) in methylene dichloride (10 ml.) to boron trichloride (2·77 g., 2 mols.) at $-50°$, followed by removal of volatile matter at 15°/15 mm., gave a residue (5·24 g.) consisting of a mixture of the chloro-esters (Found: PhO, 63·0; Cl, 27·8; B, 5·60%). With boron trichloride (3·9 mols.) a similar result was obtained.

(*b*) Triphenyl borate (3·25 g., 1 mol.) in methylene dichloride (20 ml.) was added to boron trichloride (3·48 g., 2·75 mols., *i.e.*, 0·75 mol. excess) at $-70°$. After the mixture had remained at 20° for 15 minutes to facilitate interaction and permit removal of some excess of boron trichloride, it was again cooled to $-70°$, and pyridine (3·3 g., 3·75 mols.) in pentane (50 ml.) was added slowly (2 hr.) with shaking. The mixture was stored at 20° for 40 hr. before isolation of the white precipitate of *monopyridine complex* of phenyl dichloroboronite (8·36 g., 94%) (Found: PhO, 34·2; Cl, 27·0; C_5H_5N, 31·0. $C_{11}H_{10}ONCl_2B$ requires PhO, 36·7; Cl, 28·0; C_5H_5N, 31·2%) which for analysis could be separated from accompanying pyridine–boron trichloride by hydrolysis with cold water in which the latter is insoluble (Gerrard and Lappert, *Chem. and Ind.*, 1952, 53). Recrystallisation from methylene dichloride and pentane gave the dichloroboronite complex (m. p. 98—102°) free from pyridine–boron trichloride. After

7 days, no pyridine–boron trichloride had been formed, showing that disproportionation had not occurred (Found : PhO, 34·7; Cl, 30·7; C_5H_5N, 29·6%).

Preparation of Diphenyl Chloroboronate and its Pyridine Complex.—Triphenyl borate (21·7 g., 2 mols.) in methylene dichloride (30 ml.) was added to boron trichloride (4·40 g., 1 mol.) at −70°. After being for 1 hr. at 20° to facilitate interaction in an enclosed system and to prevent loss of boron trichloride, the mixture was cooled to −70°, and pyridine (8·9 g., 3 mols.) in pentane (20 ml.) was added slowly (30 min.). A white precipitate was formed. The solvent was decanted off, and the residue, after being washed with pentane, was the *pyridine complex* of diphenyl chloroboronate (23·48 g., 68%), m. p. 116—118° (Found : PhO, 58·4; C_5H_5N, 24·2; Cl, 10·2; B, 3·40. $C_{17}H_{15}ONClB$ requires PhO, 59·7; C_5H_5N, 25·4; Cl, 11·4; B, 3·48%). The washings afforded a residue (10·5 g., 30·4%) of the crude chloroboronate complex (Found : PhO, 57·6; C_5H_5N, 20·4; Cl, 12·2%).

Disproportionation of Phenyl Dichloroboronite.—Boron trichloride (3·71 g., 3·3 mols., *i.e.*, 1·46 g. excess) at −70° was added to triphenyl borate (2·75 g., 1 mol.) also at −70°. The temperature was then allowed to rise to −15° and the pressure reduced to 0·2 mm. Boron trichloride was collected in tubes containing potassium hydroxide, the tubes being changed at intervals. The excess of trichloride was evolved in the first few minutes, but that formed by disproportionation of the dichloroboronite came over a much slower rate. Since disproportionation became progressively slower, the temperature was increased to 20° after 3·78 hr., and to 100° after 11·37 hr. The results are summarised in the Table. The residue (2·84 g.) consisted mainly of triphenyl borate (Found : PhO, 85·0; Cl, 0·43; B, 5·3%).

Time (hr.)	0·38	1·18	2·62	3·78	4·45	4·79	6·53	11·37	15·22
BCl_3 (g.)	1·46	1·71	1·89	2·02	2·38	2·56	2·94	3·15	3·53
BCl_3 (%)	30·4	46·1	51·0	54·5	64·1	69·0	79·2	84·8	95·1

Disproportionation of Diphenyl Chloroboronate.—(*a*) The chloroboronate (16·30 g., 97·5%) was prepared by the addition of triphenyl borate (14·00 g., 2 mols.) in methylene dichloride (30 ml.) to boron trichloride (2·82 g., 1 mol.) at −70°, solvent subsequently being removed at 20°/30 mm. The product gave a distillate boiling between 52°/0·05 mm., and 116°/0·2 mm. (increase in pressure attributed to trichloride in the system) which was collected in two fractions : (i) 1·86 g., b. p. 52°/0·05 mm. to 104°/0·2 mm. (Found : PhO, 73·0; Cl, 20·7%), (ii) 1·17 g., b. p. 104—116°/0·2 mm. (Found : PhO, 75·5; Cl, 19·7; B, 4·3%), these being mixtures of the two chloro-esters. The residue (13·31 g.) was mainly triphenyl borate (Found : PhO, 95·2; Cl, 0·5; B, 4·3%). Phenyl dichloroboronite (0·68 g.) was collected in an absorption tube containing potassium hydroxide (Found : PhO, 0·35 g.; Cl, 0·28 g. Calc. for 0·68 g. of $PhO{\cdot}BCl_2$: PhO, 0·36 g.; Cl, 0·27 g.). Owing to its high volatility, no boron trichloride was collected.

(*b*) Diphenyl chloroboronate (13·35 g.) was prepared by the addition of triphenyl borate (11·10 g., 2 mols.) in methylene dichloride (20 ml.) to boron trichloride (2·25 g., 1 mol.) at −70°. After 1 hr. (20°), the solvent was removed at 10 mm. The chloroboronate was then heated at 100°/100 mm. (6 hr.) and then at 150°/100 mm. (22·5 hr.), an air-condenser being fitted to allow the loss of only boron trichloride from the equilibrium mixture. The trichloride, free from chloro-ester, was collected in tubes containing potassium hydroxide; these were changed at intervals. The results were :

Time (hr.)	3	6	7·5	19·5	28·5
BCl_3 (g.)	0·145	0·156	0·306	0·451	0·458
BCl_3 (%)	6·5	6·9	13·6	20·1	20·4

The residue (12·61 g.) was a mixture of triphenyl borate and diphenyl chloroboronate (Found : PhO, 82·4; Cl, 12·1; B, 4·70%).

*Attempted Preparation of Di-*n*-butyl Phenyl Borate.*—Phenol (9·60 g., 2 mols.) in methylene dichloride (10 ml.) was added to *n*-butyl dichloroboronite (Gerrard and Lappert, *J.*, 1951, 2545) (4·62 g., 1 mol.) at −70°, and the mixture allowed to warm to 15°, whereupon hydrogen chloride [3·68 g., 99·5% according to equation (*c*)] was evolved. The mixture was divided into two parts. From one, solvent was removed at 15°/15 mm., and the liquid *compound* (7·0 g.) (Found : B, 3·94; PhO, 68·9. $C_{16}H_{19}O_3B$ requires B, 4·01; PhO, 68·9%) afforded on distillation tri-*n*-butyl borate (1·55 g., 94%), b. p. 43°/0·002 mm., n_D^{18} 1·4130 (Found : B, 4·3. Calc. for $C_{12}H_{27}O_3B$: B, 4·7%), and triphenyl borate (4·02 g., 97·5%) (Found : B, 3·9; PhO, 95·5%). To the other part (6·5 g., 1 mol.) pyridine (1·9 g., 1 mol.) in methylene dichloride (5 ml.) was added at −70°, and the mixture was kept at 15° for 14 hr. Solvent being removed, the crystalline residue, after being washed with dry ether, afforded the pyridine complex of triphenyl borate (5·23 g., 87·4%) (Found : B, 3·04; PhO, 75·4; C_5H_5N, 20·3%). The ethereal washings contained pyridine (0·6 g.), tri-*n*-butyl borate (1·17 g.), b. p. 74°/0·7 mm., and triphenyl borate (0·5 g.) (Found : B, 3·9%).

Interaction of tert.-*Butyl Alcohol* (2 *Mols.*) *with Triphenyl Borate* (1 *Mol.*).—Experiments showed that *tert.*-butyl borate could not be isolated, but that *iso*butene and di*iso*butene in approximately equal amounts (total conversion of alcohol into olefin, 96%), each identified as appropriate dibromide, and phenol were the products when triphenyl borate (13·95 g., 1 mol.) was refluxed with *tert.*-butyl alcohol (7·12 g., 2 mols.) at 140—150° for 8 hr.

Interaction of Methanol (3 *Mols.*) *and Triphenyl Borate* (1 *Mol.*).—Methanol (1·56 g., 3 mols.) and triphenyl borate (4·70 g., 1 mol.) were heated for 3 hr. at 90°. Distillation afforded: (i) trimethyl borate and methanol (1·57 g.), b. p. 47—78°/760 mm. (Found : B, 0·089 g. corresponding to 0·82 g. of trimethyl borate), and (ii) phenol (2·20 g. Calc. for 52% conversion into borate, 2·43 g.), b. p. 67°/10 mm. The residue consisted of unchanged triphenyl borate (2·41 g. Calc. for 52% conversion, 2·47 g.) (Found : B, 3·67%), b. p. 147°/0·5 mm. Yields are based on : $3MeOH + (PhO)_3B \longrightarrow (MeO)_3B + 3PhOH$.

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