# **954.** *Preparation of Phenylboron Dichloride.*

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The low yields obtained by the reaction $(PhBO)_3 + 2BCl_3 \longrightarrow 3PhBCl_2 + B_2O_3$ are due to reversibility of the reaction. Phenylboron dichloride is most conveniently prepared from tetraphenyltin and difficulties associated with the dephenylation of the easily formed intermediate, $PhSnCl_3$, are explained in terms of the strong $p_\pi$–$d_\pi$ bonding associated with aryl–metal bonds.

PHENYLBORON DICHLORIDE is a useful reagent for the preparation of a variety of organic compounds of boron. It was first prepared [1] from diphenylmercury and boron trichloride. The vapour-phase interaction of benzene and boron trichloride in the presence of palladium-black catalyst [2] has since been found to be unreliable,[3] and although its production from the same reagents and a Friedel–Crafts catalyst has been mentioned, no details were given.[4]

The reactions of boron trichloride with phenylboronic anhydride,[5] or dialkyl phenylboronate,[6] and reaction of phosphorus pentachloride with the dialkyl phenylboronate,[7-9] are not simple. The second requires the addition of ferric chloride to decompose the alkyl dichloroborinate formed, and the decomposition products hinder the separation. In the last reaction there is a tendency for phosphorus oxychloride produced to form a 1 : 1 addition complex with phenylboron dichloride, similar to that formed between phosphorus oxychloride and boron trichloride.[10]

Reaction of boron trichloride with phenylboronic anhydride has been frequently used, but the yields are low (30—40%), even when boron trichloride is used in excess. In boiling methylene dichloride the yield is not increased. Even in the absence of solvent, with complete consumption of boron trichloride (3·0 mol.), the yield was only 38%. These facts suggest that an equilibrium exists. The immediate product, other than phenylboron dichloride, has been postulated to be boron oxychloride which is known to decompose readily into boron trichloride and boric oxide.[11,12] Reaction between boric

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[1] Michaelis and Becker, *Ber.*, 1880, **13**, 58.
[2] Pace, *Atti Accad. Lincei*, 1929, **10**, 193.
[3] Ruigh *et al.*, W.A.D.C. Technical Report, 55—26, Part III.
[4] Muetterties, *J. Amer. Chem. Soc.*, 1959, **81**, 2597.
[5] Abel, Dandegaonker, Gerrard, and Lappert, *J.*, 1956, 4697.
[6] Brindley, Gerrard, and Lappert, *J.*, 1956, 824.
[7] Nielson and McEwen, *J. Amer. Chem. Soc.*, 1957, **79**, 3081.
[8] Mikhailov and Shchegoleva, *Bull. Acad. Sci. U.S.S.R., Div. of Chem. Sci.*, 1957, 1107.
[9] Mikhailov and Kostroma, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1956, 1144.
[10] Frazer, Gerrard, and Patel, *J.*, 1960, 725.
[11] Ramser and Wiberg, *Ber.*, 1930, **63**, 1136.
[12] Gerrard and Lappert, *J.*, 1955, 3084.

oxide and phenylboron dichloride (eqn. 1) is now shown to occur. The residue with n-butanol gave di-n-butyl phenylboronate (0·4 mol.) and tri-n-butyl borate (0·9 mol.).

$$B_2O_3 + 3PhBCl_2 \longrightarrow (PhBO)_3 + 2BCl_3 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

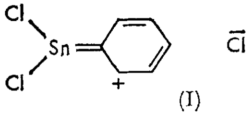
Vinylboron dichloride can be obtained [13] from tetravinyltin. We now give details of the best available preparation of phenylboron dichloride, namely, by the interaction of boron trichloride and tetraphenyltin; it can be operated on a kilogram scale by ordinary techniques.

In methylene dichloride only three of the phenyl groups could be replaced (eqn. 2), but in boiling carbon tetrachloride, 35% replacement of the fourth occurs in the stated time, whereas in the absence of solvent at reflux temperature there is nearly quantitative dephenylation of the tin (eqn. 3).

$$Ph_4Sn + 3BCl_3 \longrightarrow 3PhBCl_2 + PhSnCl_3 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$Ph_4Sn + 4BCl_3 \longrightarrow 4PhBCl_2 + SnCl_4 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

The difficulty of replacing the fourth phenyl group is probably due to the increased double-bond character ($p_\pi$–$d_\pi$ bonding) of the Ph–Sn bond in the phenyltin trichloride. Evidence for this double-bond character in tin aryls has been presented, based on calculation of the overlap integrals,[14] comparison of bond lengths,[15] and the thermodynamic dissociation constants of *p*-carboxyphenyltin compounds.[16] The ultraviolet spectrum of phenyltin trichloride has been interpreted [17] in terms of a further resonance participation by the chlorine atoms (I), and this conclusion is further supported by data on oscillator strengths.[17]



(I)

## EXPERIMENTAL

*Interaction of Phenylboronic Anhydride with Boron Trichloride.*—(i) *In methylene dichloride.* Boron trichloride (15·08 g., 3·0 mol.) at −80° was added to a suspension of phenylboronic anhydride (13·41 g.) in the solvent (100 ml.). The mixture was heated under reflux (6 hr.) (acetone–Drikold condenser). Phenylboron dichloride (6·96 g., 34%), b. p. 55—56°/7 mm. (Found: easily hydrolysed Cl, 44·6; B, 6·8. Calc. for $C_6H_5Cl_2B$: Cl, 44·6; B, 6·8%), was isolated.

(ii) *In absence of solvent.* Boron trichloride (29·17 g., 3·5 mol.) at −80° was added to phenylboronic anhydride (22·03 g.) cooled to −80°. The solid mixture slowly liquefied when warmed to room temperature, and the excess of boron trichloride refluxed. The liquid was kept at 0·1 mm. for 8 hr. to remove excess of boron trichloride (4·70 g., 0·56 mol.) which was trapped at *ca.* −180°, and then distilled into sodium hydroxide for analysis. The residue afforded phenylboron dichloride (12·85 g., 38·2%), b. p. 47°/5 mm. (Found: Cl, 44·6; B, 6·8%), and boron trichloride (8·10 g., 0·97 mol.). The distillation residue (10·91 g.) was recrystallised from benzene and water and dried (100°) to afford phenylboronic anhydride (3·72 g., 0·5 mol.) (Found: B, 10·6. Calc. for $C_{18}H_{15}O_3B_3$: B, 10·4%), which with butanol gave dibutyl phenylboronate (6·15 g.), b. p. 93—95°/0·4 mm., $n_D^{20}$ 1·4743 (Found: B, 4·5. Calc. for $C_{14}H_{23}O_2B$: B, 4·6%).

*Interaction of Phenylboron Dichloride and Boric Oxide.*—Boric oxide (3·97 g.) (freshly prepared by controlled dehydration of boric acid) and phenylboron dichloride (26·74 g., 2·95 mol.) were heated (9 hr.) at 73°/10 mm. Boron trichloride was trapped at −80°, and converted into pyridine–boron trichloride (4·08 g., 0·37 mol.). Phenylboron dichloride (13·01 g., 1·42 mol.) was recovered and redistilled (12·28 g.), b. p. 67—70°/7 mm. (Found: Cl, 44·5; B, 6·9%). The residue (8·29 g.) was recrystallised from benzene to afford a mixture of boric oxide and phenylboronic anhydride (5·19 g.) (Found: B, 21·5%), which with butanol afforded tributyl borate [12·43 g., equiv. to $B_2O_3$ (1·88 g., 0·47 mol.)], b. p. 119—124°/4 mm., $n_D^{20}$ 1·4154, and

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[13] Brinckman and Stone, *Chem. and Ind.*, 1959, 254.

[14] Craig, Maccoll, Nyholm, Orgel, and Sutton, *J.*, 1954, 332.

[15] Giacomello, *Gazzetta*, 1938, **68**, 422.

[16] Chatt and Williams, *J.*, 1954, 4403.

[17] Griffiths and Derwish, *J. Mol. Spec.*, 1959, **3**, 165.

dibutyl phenylboronate (5·83 g., 0·45 mol.), b. p. 88—90°/0·35 mm., $n_D^{20}$ 1·4722 (Found: B, 4·6%).

*Interaction of Tetraphenyltin with Boron Trichloride.*—(i) *In methylene dichloride.* Boron trichloride (52·14 g., 4·53 mol.) was added to a suspension of tetraphenyltin (42·05 g.) in the solvent (50 ml.) at −80°. The mixture was allowed to warm, and between 0° and 5° a violent reaction occurred. Matter volatile at 15 mm. was removed and trapped at −80°. The residue afforded phenylboron dichloride [42·21 g.; 90% based on eqn. (2)], b. p. 65—70°/12 mm. (Found: Cl, 44·7%), and phenyltin trichloride (10·80 g., 36·4%), b. p. 129—130°/12 mm. (Found: Cl, 35·0. Calc. for $C_6H_5Cl_3Sn$: Cl, 35·2%). The phenyltin trichloride was also identified by infrared and ultraviolet spectra. The volatile material was shown by vapour-phase chromatography to be methylene dichloride containing some boron trichloride, but free from stannic chloride.

(ii) *In carbon tetrachloride.* Boron trichloride (30·13 g.), was added to a suspension of tetraphenyltin (21·23 g.), in the solvent (50 ml.). An exothermic reaction resulted, and the mixture was then heated at 77° for 6 hr. There was a small black insoluble residue. Matter volatile at 20°/21 mm. (64·14 g.) was removed, and trapped at −80°. It afforded a series of fractions containing solvent and boron trichloride (2·32 g., 0·4 mol.) or solvent and stannic chloride (4·44 g., 0·34 mol.). The composition of the fractions was determined by chemical analysis and vapour-phase chromatography (squalane column, 80°, relative retention time of stannic chloride, 1·97 ± 0·03, of carbon tetrachloride, 1·00). The original residue (39·31 g.) afforded phenylboron dichloride [23·95 g.; 75·8% based on eqn. (3)], b. p. 70—73°/15 mm. (Found: Cl, 44·6; B, 6·8%).

(iii) *In absence of solvent.* Boron trichloride (30·57 g.) was added to tetraphenyltin (25·52 g.) at −80°. The boron trichloride, initially absorbed by the solid tetraphenyltin, began to reflux when warmed (acetone–Drikold condenser). The rate of reflux gradually increased until at approximately 5° a vigorous reaction occurred and was controlled. The product was heated at 170° under reflux for 4 hr. Distillation gave a condensate (−80°) (6·86 g.), a distillate (*a*) (15·43 g.), b. p. up to 82°/30 mm., and phenylboron dichloride (30·09 g., 79·5%), b. p. 82—86°/30 mm. (Found: Cl, 44·6; B, 6·8%). The condensate and fraction (*a*) were combined (21·14 g.) to afford a forerun (1·74 g.), b. p. up to 113°, stannic chloride (11·34 g.), b. p. 113—115° (Found: Cl, 54·4. Calc. for $Cl_4Sn$: Cl, 54·4%), and phenylboron dichloride (4·54 g., total yield 91·7%), b. p. 57—58°/10 mm. (Found: Cl, 44·6%).

NORTHERN POLYTECHNIC, HOLLOWAY ROAD, LONDON, N.7. [*Received, March* 31*st*, 1960.]