565. *The Reactions of Phenylboron Dichloride with Ethers.*

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Phenylboron dichloride did not react with ethers at 20°, but at substantially higher temperatures C–O fission was effected [except with Ph_2O and $(Cl{\cdot}CH_2{\cdot}CH_2)_2O$] to produce alkyl chloride (exclusively from the more electron-releasing of the two groups in a mixed ether) and alkyl (or aryl) phenylchloroboronite, Ph•BCl•OR. *n*-Butyl *iso*butyl ether gave a mixture of *iso*- and *tert.*-butyl chloride, and the 2-chloro-octane obtained from (–)-(ethyl 1-methylheptyl ether) was preponderantly inverted, but with much loss in activity. The results indicate that fission is preceded by carbonium-ion formation.

A new method for the preparation of phenylboron dichloride and an improved method for obtaining *tert.*-butyl *sec.*-butyl and *tert.*-butyl *iso*butyl ethers is reported.

THE reactions of boron trichloride with mixed ethers have been studied in detail.[1-6] Diaryl[5] and di-1-chloroalkyl[3] ethers did not react; di-2-chloroethyl ether formed a complex which dissociated as well as decomposed on being heated;[3] alkyl aryl ethers

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[1] Gerrard and Lappert, *J.*, 1951, 1020.
[2] *Idem, J.*, 1952, 1486.
[3] Edwards, Gerrard, and Lappert, *J.*, 1957, 377.
[4] Gerrard, Lappert, and Silver, *J.*, 1956, 4987; 1957, 1647.
[5] Colclough, Gerrard, and Lappert, *J.*, 1955, 907.
[6] Gerrard, Lappert, and Silver, *Proc. Chem. Soc.*, 1956, 19.

gave 1 : 1 complexes which decomposed to give alkyl chlorides and aryloxyboron compounds;[2] mixed dialkyl[2,3] (or alkyl allyl[4]) ethers gave unstable complexes which afforded alkyloxy(or allyloxy)-boron compounds and alkyl (or allyl) chlorides (the chlorides from the more electron-releasing of the two groups); alkyl 1-chloroalkyl ethers gave alkyl chlorides and bis-1-chloroalkyl ethers;[3] and allyl phenyl ether underwent an *ortho*-Claisen rearrangement.[6] The nature of the alkyl chloride has pointed to an S_N1 mechanism for the C–O fission,[2] and this mechanism has been supported by observations of Meerwein–Wagner[2] and allylic (S_N1')[4] rearrangements and by studies of Walden inversion.[1]

Of the alkoxy-substituted boron chlorides, the dichloroboronites, $RO{\cdot}BCl_2$ generally react similarly to the trichloride, whereas the chloroboronates, $(RO)_2B{\cdot}Cl$, generally do not react (for discussion, see ref. 7); the phenylchloroboronites, $Ph{\cdot}BCl{\cdot}OR$ are also unreactive.[8]

The phenylboron dichloride–ether system is now described. Diphenyl and bis-2-chloroethyl ethers proved unreactive. Other dialkyl ethers, unlike alkyl aryl ethers, reacted exothermally with phenylboron dichloride at 20°, but the reactants could be recovered by distillation. When the mixture was heated at about 150° for several hours, equimolar interaction took place:

$$Ph{\cdot}BCl_2 + ROR' \longrightarrow Ph{\cdot}BCl{\cdot}OR + R'Cl$$

In the case of *n*-butyl *iso*butyl ether, the *iso*butyl group gave rise to a mixture of *iso*- and *tert.*-butyl chloride (identified and analysed by gas chromatography): in no other instance was a mixture of chlorides obtained; the direction of fission is shown in the Table. The phenylchloroboronites were identified by analysis and by comparison of physical constants and infrared spectra with those obtained in previous investigations, and in some cases characterised also as 1 : 2 complexes with pyridine.[8,9] With (—)-(ethyl 1-methylheptyl ether), the 2-chloro-octane was obtained with preponderant inversion, but much racemisation.

Ether	Alkyl chloride	Ether	Alkyl chloride	Ether	Alkyl chloride
Et_2O	EtCl	Bu^iOBu^t	Bu^tCl	$Ph{\cdot}CH_2{\cdot}OMe$	$PhCH_2Cl$
$Bu^n{}_2O$	Bu^nCl	Bu^sOBu^t	Bu^tCl	$Ph{\cdot}CH_2{\cdot}OEt$	$PhCH_2Cl$
Bu^nOBu^i	Bu^iCl + Bu^tCl	Bu^sOBu^i	Bu^sCl	$Ph{\cdot}CH_2{\cdot}OBu^n$	$PhCH_2Cl$
Bu^nOBu^s	Bu^sCl	(—)-*n*-$C_6H_{13}{\cdot}CHMe{\cdot}OEt$	(+)- and (±)-*n*-$C_6H_{13}{\cdot}CHMeCl$	PhOMe	MeCl
Bu^nOBu^t	Bu^tCl			PhOEt	EtCl
				o-$C_6H_4Me{\cdot}OMe$	MeCl
				o-$C_6H_4Me{\cdot}OEt$	EtCl

Several methods are available for the synthesis of phenylboron dichloride;[7] the most successful involve interaction of boron trichloride with phenylboronic anhydride, $(Ph{\cdot}BO)_3$,[10] or phenylboronic esters,[9] or phosphorus pentachloride with phenylboronic esters.[11] We have now prepared it from phosphorus pentachloride and phenylboronic anhydride:

$$(Ph{\cdot}BO)_3 + 3PCl_5 \longrightarrow 3Ph{\cdot}BCl_2 + 3POCl_3$$

Henry[12] prepared a series of *tert.*-butyl ethers by heating a mixture of *tert.*-butyl bromide, an alcohol (Me, Et, Pr^i), and pyridine in a sealed tube. We have used this method for preparing the *tert.*-butyl *iso*- and *sec.*-butyl ether and find it superior to that of Norris and Rigby:[13]

$$Bu^tBr + ROH + C_5H_5N \longrightarrow Bu^tOR + C_5H_5N{,}HBr$$

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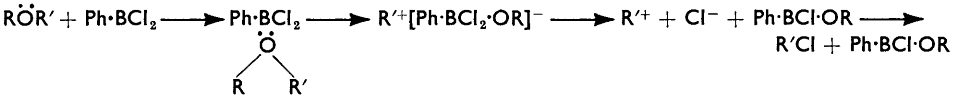
[7] Lappert, *Chem. Rev.*, 1956, **56**, 959.
[8] Dandegaonker, Gerrard, and Lappert, *J.*, 1957, 2872.
[9] Brindley, Gerrard, and Lappert, *J.*, 1956, 824, 1540.
[10] Abel, Dandegaonker, Gerrard, and Lappert, *J.*, 1956, 4697.
[11] Mikhailov and Kostroma, *Izvest. Akad. Nauk S.S.S.R. Otdel. khim. Nauk*, 1956, 376.
[12] Henry, *Bull. Acad. roy. Belg.*, 1904, 42.
[13] Norris and Rigby, *J. Amer. Chem. Soc.*, 1932, **54**, 2088.

Discussion.—The lower reactivity of phenylboron dichloride than of boron trichloride can be attributed to a lowering of Lewis-acid strength by a combination of steric and polar factors.

The lack of reaction with diphenyl and bis-2-chloroethyl ethers is considered to be due to their low Lewis-base strength because of the electron-attracting nature of the phenyl (*—M,* when attached to oxygen) and 2-chloroethyl (*—I*) groups.

Although no evidence was forthcoming to indicate the formation of a complex between the other ethers and the dichloride, the observed heat of mixing (with the dialkyl members) can be ascribed at least to association. We suggest that the fission proceeds by the following mechanism :



$$R\ddot{O}R' + Ph{\cdot}BCl_2 \longrightarrow \underset{R\quad R'}{\underset{\ddot{O}}{Ph{\cdot}BCl_2}} \longrightarrow R'^{+}[Ph{\cdot}BCl_2{\cdot}OR]^{-} \longrightarrow R'^{+} + Cl^{-} + Ph{\cdot}BCl{\cdot}OR \longrightarrow R'Cl + Ph{\cdot}BCl{\cdot}OR$$

The essential feature is the postulate of pre-ionisation (S_N1), resulting in the formation of a carbonium ion. The evidence rests on : (1) the selection of the more electron-releasing group as that found in the alkyl chloride; (2) the observation of the molecular rearrangement in the *iso*butyl system; and (3) the optical-activity data.

EXPERIMENTAL

General Procedures.—*n*-Butyl ethers of *iso-*, *sec.*- and *tert.*-butyl alcohol were obtained from *n*-butyl bromide and the appropriate sodium butoxide; *iso*butyl *sec.*-butyl ether from *iso*butyl bromide and sodium *sec.*-butoxide. The preparation of phenylboron dichloride [10] and analytical methods [8, 9, 10] have been described previously. Alkyl chlorides were identified also by comparison of infrared spectra with authentic specimens. Alkyl and aryl phenylchloroboronites were identified by analysis and comparison of physical constants and infrared spectra with those obtained in an earlier investigation.[8, 9]

Preparation of tert.*-Butyl Ethers.*—(a) iso*Butyl* tert.*-butyl.* A mixture of *iso*butyl alcohol (18·5 g., 1 mol.), *tert.*-butyl bromide (34·25 g., 1 mol.), and pyridine (19·75 g., 1 mol.) was heated in a sealed tube at 100° for 15 hr., dissolved in diethyl ether, washed with dilute hydrochloric acid, water, and sodium hydrogen carbonate, and dried (Na_2SO_4). The fraction having b. p. 108—114° was separated and redistilled from sodium, pure *iso*butyl *tert.*-butyl ether (13·76 g., 42%), b. p. 111—112°, n_D^{20} 1·3930, d_4^{20} 0·755, being obtained.

(b) sec.*-Butyl* tert.*-butyl.* By similar procedure, *sec.*-butyl alcohol (18·5 g.), *tert.*-butyl bromide (34·25 g.), and pyridine (19·75 g.) gave *sec.*-butyl *tert.*-butyl ether (3·80 g., 12%), b. p. 101—102°, n_D^{20} 1·3950, d_4^{20} 0·774.

Preparation of Phenylboron Dichloride by Phosphorus Pentachloride.—A mixture of phenylboronic anhydride [10, 13] (3·50 g., 1 mol.) and phosphorus pentachloride (7·00 g., 1 mol.) was melted (160°) and heated under reflux at 120—130° for 24 hr. Subsequent distillation afforded phosphorus oxychloride (2·04 g., 40%) as a forerun. The main fraction, after redistillation, was pure phenylboron dichloride (3·20 g., 60%), m. p. −2° to +2°, b. p. 62—63°/11 mm., n_D^{20} 1·5440 (Found : Cl, 44·1; B, 6·7. Calc. for $C_6H_5Cl_2B$: Cl, 44·5; B, 6·8%). There was a non-volatile residue (3·95 g.), which appeared to contain starting materials.

In preliminary experiments it was noted that there was no reaction below the m. p. of phosphorus pentachloride and that 24 hours' heating was the optimum.

Interaction between Phenylboron Dichloride and Ethers.—The ether (1 mol.) was added to the dichloride (1 mol.) either at −80° [in experiments (1), and (8)—(16)], or at 20° [experiments (2)—(7)]. The reaction was noted to be exothermal only in experiments (1), (2), and (7)—(13) (although in each case the reactants could at this stage be recovered nearly quantitatively from the mixture). The mixture was heated for 8—10 hr. at 60° (1), 115—125° (2 and 8—12), 150—155° (14—16), or 160—170° (3—6, and 13) (the numbers in parentheses refer to the following experiments). The products were then separated and characterised as described below.

(1) Diethyl ether (1·466 g.) and dichloride (3·15 g.). Volatile matter was removed (15 mm.)

and the residue afforded ethyl phenylchloroboronite (2·970 g., 89%), b. p. 65—68°/10 mm., n_D^{20} 1·5130 (Found : Cl, 21·6; B, 6·3. Calc. for $C_8H_{10}OClB$: Cl, 21·1; B, 6·4%).

(2) Di-*n*-butyl ether (2·673 g.) and dichloride (3·27 g.). The volatile matter (butyl chloride, b. p. 80°) was collected in a trap at −80° and the residue on distillation afforded *n*-butyl phenylchloroboronite (3·53 g., 87%), b. p. 55—56°/0·05 mm., n_D^{20} 1·5000 (Found : Cl, 18·0; B, 5·6. Calc. for $C_{10}H_{14}OClB$: Cl, 18·0; B, 5·5%), leaving a brown semisolid residue (0·15 g.).

(3) Anisole (2·2 g.) and dichloride (3·15 g.). On distillation, a forerun of anisole and phenylboron dichloride (1·74 g.), n_D^{20} 1·5330, b. p. 75—80°/14 mm., and subsequently phenyl phenylchloroboronite (1·93 g., 45·0%), b. p. 105—108°/0·05 mm., n_D^{20} 1·5775 (Found : Cl, 16·2; PhO, 43·8. Calc. for $C_{12}H_{10}BClO$: Cl, 16·4; PhO, 43·0%), were obtained. The residue (Found : B, 4·7%) did not contain chlorine.

When the experiment was carried out at room temperature phenylboron dichloride and anisole were recovered quantitatively.

(4) Phenetole (2·44 g.) and dichloride (3·24 g.). Fractional distillation afforded a forerun of low boiling material, containing phenetole and phenylboron dichloride (0·75 g.), and later pure phenyl phenylchloroboronite (2·10 g., 45·7%), b. p. 104—106°/0·05 mm., n_D^{20} 1·5780 (Found : Cl, 16·7%). A residue (1·00 g.) (Found : B, 5·0%), free from chlorine remained.

(5) Methyl *o*-tolyl ether (2·402 g.) and dichloride (3·07 g.). Distillation gave a forerun (0·67 g.) of ether and dichloride, and later *o*-tolyl phenylchloroboronite (2·1 g., 47·2%), b. p. 110—115°/0·05 mm., n_D^{21} 1·5645 (Found : Cl, 15·9; C_6H_4MeO, 44·1. Calc. for $C_{13}H_{12}BCl$: Cl, 15·4; C_6H_4MeO, 46·4%). The residue (1·24 g.) (Found : B, 4·5; C_6H_4MeO, 62·1%) did not contain chlorine and was semisolid.

(6) Ethyl *o*-tolyl ether (2·730 g.) and dichloride (3·17 g.). On distillation, there were obtained a small forerun of ether and dichloride (1·00 g.) and, as main product, *o*-tolyl phenylchloroboronite (2·15 g., 48%), b. p. 105—107°/0·05 mm., n_D^{21} 1·5660 (Found : Cl, 15·6; C_6H_4MeO, 39·4%). The semisolid, pentane-soluble residue (1·26 g.) (Found : B, 4·7; C_6H_4MeO, 65·5%) was free from chlorine.

(7) *n*-Butyl *iso*butyl ether (2·82 g.) and dichloride (3·42 g.). Distillation afforded *n*-butyl phenylchloroboronite (3·75 g., 89%), b. p. 64°/0·1 mm., n_D^{23} 1·4985 (Found : Cl, 18·1; B, 5·5%), a residue (0·20 g.), and a condensate (at −80°) comprising a mixture (1·46 g., 73%) of *iso*- (18%) and *tert.* (82%)-butyl chloride, b. p. 48—68°, n_D^{20} 1·3900 (Found as *tert.*-C_4H_9Cl : Cl, hydrolysable by cold HNO_3, 32·5; total Cl, 38·5. Calc. for C_4H_9Cl : Cl, 38·4%). The mixture of butyl chlorides was analysed by vapour chromatography.

(8) *n*-Butyl *sec.*-butyl ether (2·57 g.) and dichloride (3·13 g.). There were obtained : (*a*) *n*-butyl phenylchloroboronite (3·21 g., 83%), b. p. 59°/0·05 mm., n_D^{20} 1·4975 (Found : Cl, 18·0; B, 5·5%) ; (*b*) *sec.*-butyl chloride (1·35 g., 74%), b. p. 68—70°, n_D^{20} 1·4005 (Found : Cl, 38·1%) ; and (*c*) a non-volatile residue (0·24 g.).

(9) *n*-Butyl *tert.*-butyl ether (2·66 g.) and dichloride (3·24 g.). There were obtained *n*-butyl phenylchloroboronite (3·20 g., 80%), b. p. 62—63°/0·02 mm., n_D^{20} 1·5000 (Found : Cl, 17·9; B, 5·5%), *tert.*-butyl chloride (1·20 g., 64%), b. p. 51—51·5°, n_D^{20} 1·3915 (Found : Cl, 37·9%), and a residue (0·28 g.).

(10) *iso*Butyl *sec.*-butyl ether (2·56 g.) and dichloride (3·11 g.). There were obtained *iso*butyl phenylchloroboronite (3·37 g., 88%), b. p. 50—51°/0·01 mm., n_D^{21} 1·4900 (Found : Cl, 17·9; B, 5·4%), *sec.*-butyl chloride (1·42 g., 79%), b. p. 68—69°, n_D^{20} 1·3985 (Found : Cl, 37·8%), and a residue (0·27 g.).

(11) *iso*Butyl *tert.*-butyl ether (2·57 g.) and dichloride (3·10 g.). There were obtained *iso*butyl phenylchloroboronite (3·05 g., 95%), b. p. 50—51°/0·01 mm., n_D^{22} 1·4905 (Found : Cl, 18·1; B, 5·5%), and *tert.*-butyl chloride (1·10 g., 61%), b. p. 51—51·5°, n_D^{20} 1·3950 (Found : Cl, 37·5%).

(12) *sec.*-Butyl *tert.*-butyl ether (1·62 g.) and dichloride (1·95 g.) gave *sec.*-butyl phenylchloroboronite (1·89 g., 78%), b. p. 47—48°/0·05 mm., n_D^{22} 1·4885 (Found : Cl, 17·9; B, 5·4%), *tert.*-butyl chloride (0·78 g., 67%), b. p. 51—51·5° (Found : Cl, 38·1%), and a residue (0·25 g.).

(13) (−)-(Ethyl 1-methylheptyl ether) (3·52 g., α_D^{20} −9·96°)[15, 16] and dichloride (3·51 g.). Distillation gave a single fraction (5·15 g.) boiling over a wide range. A condensate (0·74 g.), trapped at −80°, was identified as (+)-2-chloro-octane, b. p. 51°/8 mm., n_D^{20} 1·4215, α_D^{20} +9·6°

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[14] Bean and Johnson, *J. Amer. Chem. Soc.*, 1932, **54**, 4415.
[15] Kenyon, *J.*, 1922, **121**, 2540.
[16] Kenyon and McNicol, *J.*, 1923, **123**, 14.

(Found : Cl, 23·7. Calc. for $C_8H_{17}Cl$: Cl, 23·9%). The distillate was separated chemically. Thus, pyridine (3·59 g.) in *n*-pentane (15 c.c.) was added to a portion (3·81 g.) of distillate and the mixture was set aside for 24 hr., whereafter the crystalline precipitate which had formed was filtered off, washed with *n*-pentane and dried. This precipitate (equiv. to 78% yield of Ph·BCl·OEt) was identified as the pyridine complex of ethyl phenylchloroboronite, m. p. 106—110° (Found : Cl, 10·2; B, 3·3; C_5H_5N, 48·6. Calc. for $C_8H_{10}OClB,2C_5H_5N$: Cl, 10·9; B, 3·3; C_5H_5N, 48·4%). The *n*-pentane extracts were combined and on removal of solvent gave further (+)-2-chloro-octane (1·65 g., total 76%), b. p. 53—54°/8 mm., n_D^{20} 1·4270, α_D^{20} +9·6° (Found : Cl, 23·2%).

(14) Benzyl methyl ether (2·34 g.) and dichloride (3·04 g.). Fractionation proved difficult and the entire mixture was dissolved in diethyl ether, washed with sodium hydroxide and water, and dried (Na_2SO_4). Distillation then afforded benzyl chloride (1·6 g., 65%), b. p. 67—67·5°/11 mm., n_D^{20} 1·5400 (Found : Cl, 28·4. Calc. for C_7H_7Cl : Cl, 28·1%) (*p*-nitro-derivative, m. p. 70°).

In a second experiment, on the same scale, the aqueous treatment was replaced by addition of pyridine in *n*-pentane. There was obtained the crude, semisolid pyridine complex of methyl phenylchloroboronite, m. p. 95—105° (Found : Cl, 11·0; B, 3·4. Calc. for $C_7H_8OClB,2C_5H_5N$: Cl, 11·4; B, 3·5%).

(15) Benzyl ethyl ether. A procedure similar to (14), in one experiment (water treatment), gave benzyl chloride (71%), b. p. 60—61°/10 mm., n_D^{20} 1·5400 (Found : Cl, 27·7%) (*p*-nitro-derivative, m. p. 70°). In another experiment (pyridine treatment), there was obtained the pyridine complex of ethyl phenylchloroboronite (72%), m. p. 100—106° (Found : Cl, 10·1; B, 3·3; C_5H_5N, 48·5%).

(16) Benzyl *n*-butyl ether (3·18 g.) and dichloride (3·12 g.). Fractional distillation afforded : (*a*) benzyl chloride contaminated with the ether and dichloride (2·26 g.), b. p. 80—90°/10 mm., n_D^{20} 1·5195; (*b*) crude *n*-butyl phenylchloroboronite (2·38 g.), b. p. 60—66°/0·01 mm., n_D^{20} 1·5045 (Found : Cl, 14·1; B, 5·6%); and (*c*) a residue (1·05 g.). Fraction (*a*) was given aqueous treatment and fraction (*b*) pyridine treatment, as described in (14). From (*a*) there was obtained benzyl chloride (1·40 g., 89%), b. p. 67—68°/13 mm., n_D^{20} 1·5410 (*p*-nitro-derivative, m. p. 70°). From (*b*) there was obtained the pyridine complex of *n*-butyl phenylchloroboronite, m. p. 105—110° (Found : Cl, 10·3; B, 3·0; C_5H_5N, 44·0. Calc. for $C_{10}H_{14}OClB,2C_5H_5N$: Cl, 10·0; B, 3·1; C_5H_5N, 44·6%).

(17) Diphenyl and di-2-chloroethyl ether severally. The reactants were recovered almost quantitatively after an equimolecular mixture of each ether and the dichloride had been heated at 150—165° for 10 hr.

We thank Mr. H. Pyszora for carrying out the infrared spectral measurements, and the National College of Rubber Technology (Northern Polytechnic) for providing the facilities for these.

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[*Received, March* 14*th*, 1957.]