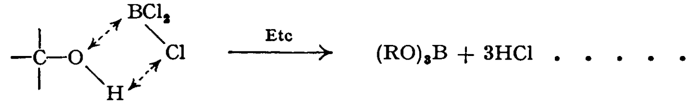
226. *Interaction of Boron Trichloride with Optically Active Alcohols and Ethers.*

By W. GERRARD and M. F. LAPPERT.

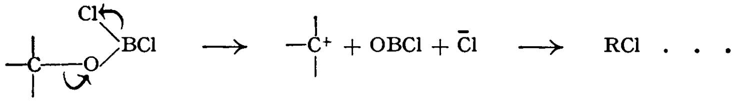
Boron trichloride and (+)-octan-2-ol gave (+)-tri-2-octyl borate and considerably racemised (—)-2-chloro-octane, the proportion of the latter increasing, so that it became the main product as the proportion of the trichloride was increased. Similarly (+)-1-phenylethanol afforded the (+)-1-chloro-1-phenylethane and (+)-tri-1-phenylethyl borate, completely racemised chloride being the main product when the proportion of the trichloride was increased. However, the trichloride readily caused racemisation of the 1-chloro-1-phenylethane itself. Both tri-esters readily interacted with the trichloride and afforded the corresponding alkyl chloride. Hydrogen chloride and hydrogen bromide were without action on the (+)-tri-2-octyl borate at 15°, but readily effected the dealkylation of (+)-tri-1-phenylethyl borate, the halide formed tending to have preponderantly retained configuration. (—)- and (±)-2-Chloro-octane and (±)-1-chloro-1-phenylethane were obtained by fission of the corresponding ethyl ethers, by means of the trichloride, the boron atom being found in the isolated ethoxyboron dichloride in both cases. Probable mechanisms are suggested.

SUCCESSIVE replacement of the chlorine atoms in boron trichloride by interaction with methyl and ethyl alcohols at —60° was effected by Wiberg and Sütterlin (*Z. anorg. Chem.*, 1931, **202**, 1, 22, 31). Kinney, Thompson, and Cheney (*J. Amer. Chem. Soc.*, 1935, **57**, 2396) prepared di*iso*amyloxyboron chloride in 15% yield from the alcohol and trichloride, but by proportionation between the latter and tri-ester the yield was 45%.

A study of the interactions between boron trichloride and optically active alcohols has been undertaken in order to elucidate the nature and sequence of reactions occurring between alcohols and inorganic non-metallic halides. (+)-Octan-2-ol and (+)-1-phenylethanol were examined first, because the alcoholic carbon atom in the former may be considered as having a normal degree of reactivity, whereas in the latter the reactivity is much greater, owing to the polarisability of the phenyl group. Previous work shows that these alcohols are very convenient reference compounds. The results of our experiments are recorded in the table. There is a marked contrast between the reactions of (+)-octan-2-ol with boron trichloride, on the one hand, and with phosphorus halides (Gerrard, *J.*, 1944, 85; 1945, 848; 1946, 741) and silicon tetrachloride (Gerrard and Woodhead, *J.*, 1951, 519), on the other. With 3 mols. of (+)-alcohol to 1 mol. of trichloride the main product was (+)-tri-2-octyl borate and the subsidiary product was much-racemised (—)-2-chloro-octane, the latter becoming the main product as the relative proportion of trichloride was increased. The alkoxyboron chlorides, $B(OR)Cl_2$ and $B(OR)_2Cl$, could not be isolated.

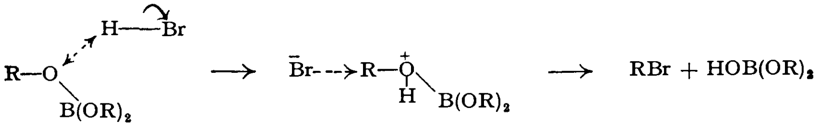


$$\xrightarrow{\text{Etc}} (RO)_3B + 3HCl \quad \ldots\ldots \quad (1)$$



$$\longrightarrow \ -\overset{|}{\underset{|}{C}}{}^{+} + OBCl + \bar{C}l \longrightarrow RCl \quad \ldots \quad (2)$$

The tri-ester was probably formed by three successive four-centre broadside approaches (1), whereas the formation of much racemised alkyl chloride was probably due to the pronounced electrophilic activity of the boron atom, further accentuated by the electron attraction of the chlorine atoms, as shown in (2). The greater the proportion of alcohol with respect to trichloride, the greater the chance that mechanism (1) will lead to the tri-ester. As hydrogen chloride failed to produce alkyl chloride when passed into the tri-ester, it is not likely to be responsible for formation of alkyl chloride in the alcohol–trichloride system. Furthermore, even hydrogen bromide at 100° did not react rapidly, and then the formation of 2-bromo-octane was accompanied by inversion without significant loss in rotatory power. The mechanism in this case would appear to be that depicted in (3). Formation of much racemised (−)-2-chloro-octane from (+)-tri-ester and trichloride probably entails proportionation to the chloro-esters followed by decomposition according to (2).

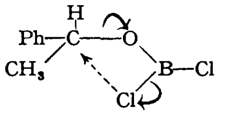

(3)

Pyridine facilitated the broadside mechanism (1), presumably by virtue of the hydrogen bond, $RO\cdot H{:}NC_5H_5$ (Gerrard, *J.*, 1939, 99); but in pentane solution the yield of (+)-tri-ester was only 64%, because some pyridine and trichloride were diverted to the complex, $Cl_3B{:}NC_5H_5$. When the reagents were mixed in chloroform, however, the yield of tri-ester was increased to 85%. We conclude that this complex was not necessary for the production of tri-ester, because when the complex (prepared by mixing pyridine and the trichloride in pentane) was kept in pentane containing the requisite amounts of (+)-octan-2-ol and pyridine, there was a very slow conversion into pyridine hydrochloride even when the mixture was heated. The reagents (including the complex) being dissolved in chloroform, there was likewise a slow conversion at 15°; but after the mixture had been heated, the (+)-tri-ester was obtained in 84% yield. If, in the examples of certain alcohols, the tri-ester can be made more conveniently by boron trichloride and pyridine than by reagents previously used, the complex would serve equally well, and would be a convenient form in which to store the trichloride.

Reagents. (Numbers preceding formulæ refer to molecular proportions.)	Products.	Yield, %.	a_D.	Steric effect.*
R = 2-*Octyl*.				
3(+)-ROH (+7·7°), 1BCl_3	(−)-RCl	9	−6·7°	I + much Ra
	(+)-B(OR)$_3$	83	+28·3	—
1 ,, ,, ,,	RCl	87	—	Ra
1 ,, ,, 2BCl_3	(−)-RCl	97	−6·2	I + much Ra
3 ,, ,, 1BCl_3 (with pyridine in pentane)	(+)-B(OR)$_3$	64	+28·0	—
Repeated in chloroform	,,	85	+28·0	—
3(+)-ROH (+3·1°), 1$C_5H_5N{:}BCl_3$, 2C_5H_5N in hot $CHCl_3$)	(+)-B(OR)$_3$	84	+11·9	—
(+)-B(OR)$_3$ (+28·0°), HBr (100°)	(−)-RBr	86	−37·4	I
,, ,, HI (15°)	(−)-RI	60	−45·2	I + some Ra
1(+)-B(OR)$_3$ (+30·0°), 1·9BCl_3	(−)-RCl	93	−10·6	I + much Ra
1(+)-ROEt (+5·3°), >1BCl_3	(−)-RCl	98	− 3·1	I + much Ra
	$BCl_2\cdot OEt$	87	—	—
R = 1-*Phenylethyl*.				
3(+)-ROH (+21·6°), 1BCl_3	(+)-RCl	50·1	+20·0	Re + Ra
	(+)-B(OR)$_3$	24·2	+21·6	—
1(+)-ROH (+32·4°), 1·2BCl_3	RCl	87	—	Ra
3(+)-ROH (+28·4°), 1BCl_3, 3C_5H_5N in pentane	(+)-RCl	—	+26·0	Re + Ra
	(+)-B(OR)$_3$	69	+28·0	—
3(+)-ROH (32·4°), 1BCl_3, 3C_5H_5N in $CHCl_3$	(+)-B(OR)$_3$	86	+32·4	—
3(+)-ROH (+32·0°), 1$C_5H_5N{:}BCl_3$, 2C_5H_5N in hot $CHCl_3$	(+)-B(OR)$_3$	88	+29·8	—
(+)-(RO)$_3$B (+31·0°), HCl	(+)-RCl	94	+13·0	Re + much Ra
,, (+30·0°), HCl (Repeat)	(+)-RCl	—	+8·0	Re + much Ra
+)-(RO)$_3$B (+31·0°), HBr	(−)-RBr	74	−7·6	I + much Ra
,, (+30·0°), HBr (Repeat)	(+)-RBr	—	+2·4	Re + much Ra
(+)-(RO)$_3$B (+28·0°), BCl_3	RCl	80	—	Ra
(+)-ROEt (+58·5°), BCl_3	RCl	—	—	Ra
	$BCl_2\cdot OEt$	78	—	—

* Re = retention. I = inversion of configuration. Ra = racemisation.

With reference to (+)-1-phenylethanol, the special feature was the formation of (+)-1-chloro-1-phenylethane accompanied by some retention of configuration, when 1 mol. of trichloride was used for 3 mols. of alcohol. A suggested mechanism (4) is similar to that formulated for the formation of (+)-1-chloro-1-phenylethane from the (+)-alcohol through the agency of thionyl chloride (McKenzie and Clough, *J.*, 1913, **103**, 687), and designated S_Ni by Cowdrey, Hughes, Ingold, Masterman, and Scott (*J.*, 1937, 1252). Loss of rotatory power could be due to the concurrent operation of mechanism (2). It is clear that some molecules of the chloro-ester react by continuation of mechanism (1), because the (+)-tri-ester was also isolated. As the proportion of trichloride was increased so the yield of alkyl chloride was increased, but racemisation became extensive. It is noteworthy that 1-chloro-1-phenylethane itself (in



$\longrightarrow$ RCl + OBCl . . . . (4)

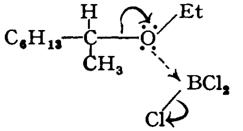
contrast to 2-chloro-octane) was readily racemised by the trichloride, presumably owing to the combined effect of the polarisability of the phenyl group and the electrophilic tendency of the boron atom, thus :

$$\mathrm{R}\overset{\curvearrowright}{—}\mathrm{Cl}{\dashrightarrow}\mathrm{BCl_3} \longrightarrow \overset{+}{\mathrm{R}} + \overset{-}{\mathrm{Cl}}\mathrm{BCl_3} \longrightarrow \text{(racemised) RCl} + \mathrm{BCl_3}.$$

(+)-Tri-1-phenylethyl borate was readily dealkylated by hydrogen chloride, and still more readily by hydrogen bromide, there being very considerable loss in activity, but a tendency towards preponderant retention of configuration. Values of rotatory power quoted in the table should be compared with the following maximum values (Gerrard, *loc. cit.*) for α_D^{18} (l = 10 cm.) : RCl, 99°; RBr, 131°.

Phenomena related to the formation of the complex, $Et_2O{:}BCl_3$, and to its subsequent fission at the Et–O bond were described by Ramser and Wiberg (*Ber.*, 1930, **63**, 1136) and Wiberg and Sütterlin (*loc. cit.*). More recently, Benton and Dillon (*J. Amer. Chem. Soc.*, 1942, **64**, 1128) heated eight different ethers with boron tribromide and determined the fate of each hydrocarbon member of the ether. The mixed ethers with one exception were phenolic, and only one mol. of tribromide was used for three of the ether being treated. In our experiments we used more than one mol. of trichloride for each mol. of ether.

Ethyl (+)-2-octyl ether afforded ethoxyboron dichloride in 87%, and (−)-2-chloro-octane in 98% yield. Again, the mechanism must account for preponderant inversion with considerable loss in activity, and that suggested is shown in (5). It is clear that fission has occurred in accordance with the greater electron release of the secondary group. It is not surprising that ethyl (−)-1-phenylethyl ether afforded ethoxyboron dichloride and racemised 1-chloro-1-phenylethane.



$\longrightarrow$ $\mathrm{EtO{\cdot}BCl_2} + \overset{+}{\mathrm{R}} + \overset{-}{\mathrm{Cl}}$ $\longrightarrow$ RCl . . . (5)

The possibility should be borne in mind of a one-transition-state approach of the reagents, resulting in direct attachment of a chlorine atom to the reactive carbon atom. In these reactive systems, the energy possessed by the molecules at the moment of effective collision might influence the precise course of electronic rearrangement. The formation of an intermediate compound brings into play the consideration of the different ways in which it can effect the ultimate attachment of the chloride atom.

EXPERIMENTAL.

It is stated when reaction mixtures were treated with water. Rotatory powers are recorded for *l* = 10 cm.

Interaction of (+)-Octan-2-ol and Boron Trichloride.—The alcohol (4·8 g., 1 mol.; α_D^{15} +7·7°) was added dropwise to boron trichloride (1·8 g., 0·33 mol.) at −10°, and during the ensuing vigorous reaction hydrogen chloride (0·85 g.) was evolved. On distillation, (−)-2-chloro-octane (0·5 g.), b. p. 63°/16 mm., α_D^{15} −6·7° (Found : Cl, 23·8. Calc. for $C_8H_{17}Cl$: Cl, 23·9%), and *tri-2-octyl borate* (4·1 g.), b. p. 148°/0·5 mm., α_D^{15} +28·3°, n_D^{22} 1·4280, d_4^4 0·8642 (Found : C, 72·6; H, 12·6; B, 2·9. $C_{24}H_{51}O_3B$ requires C, 72·4; H, 12·8; B, 2·7%), were obtained. (+)-Octan-2-ol (1·2 g.), α_D^{15} +7·7°, was obtained from the tri-ester (1·43 g.) by steam-distillation in the presence of potassium hydroxide. In a similar way, 1 mol. of the trichloride and the alcohol (3·25 g., 1 mol.) afforded racemised 2-chloro-octane (3·2 g.), b. p. 60°/13 mm. (Found : Cl, 23·1%), and a residue which with water gave boric acid (1·30 g.) whereas, when 2 mols. of trichloride were used, the corresponding data were : 2-chloro-octane (3·6 g.), α_D^{15} −6·2° (Found : Cl, 23·6%), and boric acid (1·37 g.).

The trichloride (2·0 g., 1 mol.) in *n*-pentane (10 c.c.) was added to (+)-octan-2-ol (6·7 g., 3 mols.; α_D^{20} +7·7°) and pyridine (4·0 g.,3 mols.) in pentane (25 c.c.) at −10°. After 2 hours the white precipitate (5·2 g.) formed during the addition was separated and found to consist of pyridine hydrochloride (4·2 g.)

(Found: Cl, 30·5; C_5H_5N, 68·2. Calc.: Cl, 30·7; C_5H_5N, 68·4%) and a water-insoluble substance (1·0 g.), probably pyridine–boron trichloride, m. p. 115° (Found: Cl, 50·5; B, 6·5; C_5H_5N, 43·9%). On distillation, the pentane solution afforded pyridine (0·6 g.), b. p. 30°/20 mm., (+)-octan-2-ol (2·5 g.), b. p. 78°/15 mm., α_D^{20} +7·7°, and (+)-tri-2-octyl borate (4·3 g., 64%), b. p. 148°/0·5 mm., α_D^{20} +28·0° (Found: B, 2·72%). When the pentane filtrate was washed with water before distillation, the yield of tri-ester was reduced owing to hydrolysis.

We could find no way of purifying the substance we believe to be pyridine–boron trichloride, but by the interaction of boron trichloride and pyridine itself in pentane solution at −10° Dr. H. J. S. King obtained a white microcrystalline product which was doubtless *pyridine–boron trichloride*, m. p. 114·5—115° (Found: C, 30·6; H, 2·6; Cl, 53·8; N, 7·1; B, 5·7. C_5H_5N,BCl_3 requires C, 30·6; H, 2·6; Cl, 54·2; N, 7·1; B, 5·5%).

The yield of the tri-ester was increased to 85% by conducting the operation in chloroform, from which no precipitate was obtained when the trichloride (3·4 g., 1 mol.) was added to the (+)-alcohol (11·0 g., 3 mols.) and pyridine (6·7 g., 3 mols.) in the solvent (45 c.c. total volume) at −10°. The solid which remained on evaporation of the solvent in a vacuum at room temperature was leached with successive amounts of pentane, and the final residue (9·84 g.) consisted of pyridine hydrochloride (9·44 g.) and the water-insoluble substance (0·4 g.), m. p. 115°. Distillation of the pentane extract afforded octan-2-ol (1·5 g.), b. p. 78°/15 mm., and tri-2-octyl borate (9·4 g.), b. p. 148°/0·5 mm., α_D^{20} +28·0° (Found: C, 71·9; H, 13·0; B, 2·7. Calc. for $C_{24}H_{51}O_3B$: C, 72·4; H, 12·8; B, 2·72%).

Further to compare the effects of the two solvents mentioned, the reagents were mixed as described, and after the stated time the solvent was removed in a vacuum at room temperature. The solid residue was transferred to a sintered-glass crucible and extracted with water. The chloride ion found in the extract being assumed to be equivalent to pyridine hydrochloride, and this equivalent to the tri-ester produced, we concluded that in pentane the yield of tri-ester was 76·1% after 2 hours, and 79·5% after 24 hours; in chloroform solution, the yield was 90·9 after 2 hours, and 91·8% after 48 hours.

Interaction of Pyridine–Boron Trichloride and Octan-2-ol in the Presence of Pyridine.—(+)-Octan-2-ol (4·42 g., 3 mols.; α_D^{20} +3·1°), pyridine (1·78 g., 2 mols.), and pyridine–boron trichloride (2·21 g., 1 mol.) (prepared from pyridine and the trichloride) were heated under reflux in chloroform solution for 4 hours. After removal of the solvent in a vacuum, the residue was leached with pentane, and the final solid residue consisted of pyridine hydrochloride (3·87 g.) (Found: Cl, 30·1; C_5H_5N, 68·0%) and unchanged boron complex (0·1 g.), m. p. 114°. On distillation, the pentane solution afforded (+)-octan-2-ol (0·2 g.), α_D^{20} +3·1°, and (+)-tri-2-octyl borate (3·8 g.), b. p. 156°/1 mm., α_D^{20} +11·9° (Found: C, 72·7; H, 13·0; B, 2·70%). When the reagents were kept in chloroform at room temperature, the conversion into tri-ester was very slow—only 1% in 48 hours. In pentane the conversion was slow; even after the mixture had been heated under reflux for 6 hours the yield was only 9·8%.

Interaction of Boron Trichloride and 1-*Phenylethanol.*—The trichloride (2·0 g., 1 mol.) in pentane (10 c.c.) was added to (+)-1-phenylethanol (6·1 g., 3 mols.; α_D^{20} +21·6°) in pentane (10 c.c.) at −10°. Some unreacted alcohol separated, but when the mixture was shaken at room temperature the separate layer disappeared, a precipitate formed, and hydrogen chloride was evolved. On distillation, (+)-1-chloro-1-phenylethane (3·6 g.), b. p. 76°/14 mm., α_D^{20} +20·0° (Found: Cl, 25·0. Calc.: Cl, 25·3%), (probably) (+)-di-1-phenylethyl ether (0·7 g.), b. p. 110°/0·3 mm., α_D^{20} +56·8° (Found: C, 85·5; H, 7·9. Calc. for $C_{16}H_{18}O$: C, 85·0; H, 8·0%), and (+)-tri-1-phenylethyl borate (1·5 g.), b. p. 174°/0·2 mm., α_D^{20} +21·6° (Found: B, 2·84. Calc.: B, 2·89%) (see later), were obtained. When 1·2 mols. of trichloride and 1·0 mol. of alcohol, α_D^{20} +32·4°, were used, racemised 1-chloro-1-phenylethane (87% yield), b. p. 77°/18 mm. (Found: Cl, 25·1%), was obtained.

It was shown that 1-chloro-1-phenylethane is readily racemised in contact with boron trichloride. After the former, α_D^{20} +27·6° (3·0 g.), had been in contact with the latter (1·8 g.) in pentane (10 c.c.) for 1 hour at 15°, (±)-1-chloro-1-phenylethane (2·9 g., 97%), b. p. 80°/20 mm. (Found: Cl, 25·4%), was isolated. Under similar conditions, even after 24 hours, (+)-2-chloro-octane showed no change in rotatory power.

Boron trichloride (3·5 g., 1 mol.) in pentane (10 c.c.) was added to (+)-1-phenylethanol (10·5 g., 3 mols., α_D^{20} +28·4°) and pyridine (6·9 g., 3 mols.) in pentane (35 c.c.) at −10°. After 4 hours at 15°, a lower semi-solid layer was washed with ether, the washings being added to the upper layer, and the solid residue consisted of pyridine hydrochloride (6·4 g.) (Found: Cl, 30·0; C_5H_5N, 67·8%) and pyridine–boron trichloride (0·3 g.), m. p. 115°. From the ethereal solution, (+)-1-chloro-1-phenylethane (2·5 g.), b. p. 80°/20 mm., α_D^{20} +26·0° (Found: Cl, 25·0%), (+)-1-phenylethanol (2·0 g.), b. p. 90°/20 mm., α_D^{20} +28·3°, and (+)-*tri*-1-*phenylethyl borate* (7·2 g., 69%), b. p. 175°/0·5 mm., α_D^{20} +28·0° (Found: C, 77·7; H, 7·7; B, 2·85. $C_{24}H_{27}O_3B$ requires C, 77·0; H, 7·2; B, 2·87%), were obtained. When the operation was conducted in chloroform, the tri-ester, b. p. 170—174°/0·4 mm., α_D^{20} +32·8° (from alcohol; α_D^{20} +32·4°) (Found: C, 77·2; H, 7·5; B, 2·96%), was obtained in 86% yield.

On steam-distillation from an aqueous solution of potassium hydroxide, the (+)-alcohol (0·9 g.), α_D^{20} +32·1°, was obtained from the tri-ester (1·076 g.), α_D^{20} + 32·8°.

As described above, pyridine–boron trichloride (1.706 g., 1 mol.), pyridine (1·37 g., 2 mols.), and (+)-1-phenylethanol (3·18 g., 3 mols.; α_D^{20} +32·0°) were heated under reflux in chloroform (15 c.c.) for 3 hours. The solvent was evaporated in a vacuum, and the final residue after extraction with pentane was pyridine hydrochloride (2·97 g.) (Found: Cl, 30·5; C_5H_5N, 68·2%). Distillation of the pentane solution afforded (+)-tri-1-phenylethyl borate (2·8 g., 88%), b. p. 173°/0·2 mm., α_D^{20} +29·8° (Found B, 2·86%).

Interaction of Hydrogen Halides and Tri-esters.—Tri-2-octyl borate was recovered unchanged in amount and rotatory power after hydrogen chloride had been passed into it for 2 hours at 15°. Similarly, hydrogen bromide had no noticeable action at this temperature, but when passed for at least 16 hours at 100—110° it afforded (—)-2-bromo-octane (3·8 g.) (from 3·10 g. of tri-ester, α_D^{20} +28·0°), b. p. 74°/15 mm., α_D^{20} —37·4° (Found: Br, 41·4. Calc.: Br, 41·4%). When hydrogen iodide was passed into the tri-ester (1·32 g.) for 5 hours at 15°, (—)-2-iodo-octane (1·4 g.), b. p. 85°/15 mm., α_D^{20} —45·2° (Found: I, 51·8. Calc.: I, 52·9%), was formed.

Boric acid was precipitated when dry hydrogen chloride was passed into (+)-tri-1-phenylethyl borate (1·9 g., α_D^{20} +31·0°) for 3 hours at 15°. (+)-1-Chloro-1-phenylethane (2·0 g., 94%), b. p. 68—69°/10 mm., α_D^{20} +13·0° (Found: Cl, 25·5. Calc.: Cl, 25·3%), and boric acid (0·310 g. Calc.: 0·310 g.) were isolated. In a similar way the same ester (1·41 g.) and hydrogen bromide afforded (—)-1-bromo-1-phenylethane (1·6 g.), b. p. 90°/15 mm., α_D^{20} —7·6° (Found: Br, 43·5. Calc.: Br, 43·3%), and a residue of boric acid (0·203 g.).

Interaction of Trichloride and Tri-esters.—(+)-Tri-2-octyl borate (2·3 g., 1 mol.; α_D^{20} +30·0°) (from the alcohol, α_D^{20} +7·96°) in pentane (5 c.c.) was added to the trichloride (1·3 g., 1·9 mols.) in pentane (5 c.c.) at —10°. From the mixture, (—)-2-chloro-octane (2·4 g., 93%), b. p. 59—60°/13 mm., α_D^{20} —10·6° (Found: Cl, 23·8. Calc.: Cl, 23·9%), was obtained. Similarly, completely racemised 1-chloro-1-phenylethane (2·8 g.), b. p. 77°/15 mm. (Found: Cl, 25·4%), was obtained from the tri-ester (2·8 g., 1 mol.; α_D^{20} +28·0°) and the trichloride (1·8 g., 2 mols.).

Interaction of Boron Trichloride with Ethyl (+)-1-*Phenylethyl Ether.*—(—)-1-Chloro-1-phenylethane, α_D^{20} —86·6° (Gerrard, *J.*, 1946, 741), was converted into the ether, b. p. 76—78°/20 mm., α_D^{20} +58·5° (Found: C, 80·4; H, 9·5. Calc. for $C_{10}H_{14}O$: C, 80·0; H, 9·4%), by Hughes, Ingold, and Scott's method (*J.*, 1937, 1201). The ether (3·3 g., 1 mol.) was added to the trichloride (2·6 g., 1 mol.) at —10°. After one hour distillation afforded ethoxyboron dichloride (2·2 g., 78%), b. p. 78—80° (Found: Cl, 55·3; B, 8·52. Calc. for $C_2H_5OCl_2B$: Cl, 55·9; B, 8·53%), and a residue (2·8 g.) which was mixed with water and extracted with ether. From the dried ethereal extract, completely racemised 1-chloro-1-phenylethane (1·0 g.), b. p. 74°/12 mm. (Found: Cl, 25·0%), and a non-distillable oil (1·6 g.) were obtained.

The trichloride (5·0 g., >1 mol.) and ethyl (+)-2-octyl ether (2·6 g.; α_D^{20} +5·3°; prepared by Kenyon and McNicol's Method, *J.*, 1923, **123**, 14) were mixed at —10°, and the mixture was set aside for 2 hours. Distillation afforded ethoxyboron dichloride (1·8 g., 87%), b. p. 78—80° (Found: Cl, 56·1; B, 8·53. Calc. for $C_2H_5OCl_2B$: Cl, 55·9; B, 8·53%), and (—)-2-chloro-octane (2·8 g., 98%), b. p. 60—61°/13 mm., α_D^{20} —3·1° (Found: Cl, 23·6. Calc.: Cl, 23·9%).

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