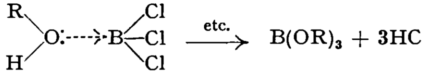
135. *Reaction Sequences in Alcohol–Boron Trichloride–Pyridine Systems.*

By M. F. LAPPERT.

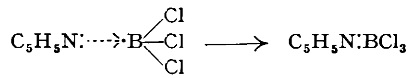
Addition of boron trichloride (1 mol.) to alcohols (the isomeric butanols, octan-1-ol, octan-2-ol, and 1-phenylethanol) (3 mols.) in presence of pyridine (3 mols.) at −10° and −80° instantly gave good yields of the trialkyl borates and pyridine hydrochloride, but little pyridine–boron trichloride. Borate formation on use of the last reagent (1 mol.), *n*-butanol (3 mols.), and pyridine (2 mols.) was much slower even at +80°. Addition of pyridine (1 mol.) to *n*-butyl dichloroboronite (1 mol.) gave a complex, $C_5H_5N,B(OR)Cl_2$, of similar stability to that of the ester itself. This type of complex was also formed by the interaction of alcohols (*n*- and *tert.*-butanol, octan-1-ol, octan-2-ol, and 1-phenylethanol) (1 mol.) with pyridine–boron trichloride (1 mol.) and decomposed to the trialkyl borates and on stronger heating to alkyl chlorides and pyridine–boron oxychloride. Possible mechanisms are discussed.

ADDITION of a non-metal halide to alcohols in the presence of pyridine has become one of the most valuable methods for the preparation of ortho-esters of these non-metals [$MX_n + nROH + nC_5H_5N \longrightarrow M(OR)_n + nC_5H_5N,HX$]. The mechanism of the reactions, and in particular the function of the pyridine, has given rise to much speculation. The more important of these suggestions are now considered for the case where the halide is boron trichloride.

Gerrard suggested (*J.*, 1939, 99; 1940, 218) that the pyridine is combined with alcohol (ROH) by virtue of hydrogen bonding, affording the compound ROH,NC_5H_5, and it is this which in turn reacts with the non-metal halide. Reactions with boron trichloride give evidence for this view. It has been shown that reactions (1) (Gerrard and Lappert, *J.*, 1951, 1020, 2545) and (2) (*ibid.*, p. 1020; *Chem. and Ind.*, 1952, 53) are very rapid. The addition of boron trichloride to an equimolecular mixture of an alcohol and pyridine involves competition between reactions (1) and (2) but, contrary to the expectation that the stronger base, pyridine, would dominate the situation, almost no pyridine–boron trichloride was isolated. The main products of the reaction were the trialkyl borate and pyridine hydrochloride in nearly quantitative yields, particularly when such a solvent was used as to afford the maximum homogeneity on mixing (see Table 1). The almost complete absence of (2) indicates that on addition of boron trichloride to the alcohol–pyridine mixture, the lone pair on the nitrogen atom is no longer available for reaction, such as would be the case if an ROH,NC_5H_5 complex were formed, whereas the oxygen lone-pair is still available for reaction. This is also in agreement with Cleverdon and Smith's dipole-moment work (*Chem. and Ind.*, 1948, 29).



$$\begin{matrix}R\\H\end{matrix}\!>\!O\!:\cdots\!\rightarrow\!BCl_3 \xrightarrow{\text{etc.}} B(OR)_3 + 3HCl \quad . \ . \ . \ . \ . \ . \ . \ . \quad (1)$$



$$C_5H_5N\!:\cdots\!\rightarrow\!BCl_3 \longrightarrow C_5H_5N\!:\!BCl_3 \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad (2)$$

It might be suggested that the first step in the interaction of boron trichloride with alcohols in the presence of pyridine is the formation of a complex intermediate between the trichloride and the base, *i.e.*, C_5H_5N,BCl_3, and that this then reacts with the alcohol to give the borate. Such a theory was put forward for the phosphorus pentachloride system (Hückel and Pietrzok, *Annalen*, 1939, **540**, 250) and the phosphorus oxychloride system (Boyd and Ladhams, *J.*, 1928, 215). That this view is not tenable in the boron trichloride system was demonstrated by showing that the pyridine complex (a stable white solid) reacts to a negligible extent with *n*-butanol in the presence of pyridine in chloroform at 25°, and only slowly at 80° (see Table 3) and thus the complex can play no significant part under normal reaction times (30 min.) and temperatures (−10° or −80°) in the main reaction.

Finally, a view that requires consideration is that the pyridine may facilitate the decomposition of a chloro-ester formed as an intermediate. This was suggested for certain thionyl chloride reactions (Kenyon, Phillips, and Taylor, *J.*, 1931, 382), particularly those which produced alkyl halide. In the boron trichloride system, however, a very different situation exists because the boron atom in an alkyl dichloroboronite has an outer shell of only six electrons and this, together with the dissymmetry of the molecule, makes for considerable instability (Gerrard and Lappert, *loc. cit.*). The addition of pyridine (1 mol.) to *n*-butyl dichloroboronite (1 mol.) afforded a co-ordination complex, the stability of which was no less than that of the chloro-ester itself.

Reactions with Pyridine–Boron Trichloride.—In an earlier paper (Gerrard and Lappert, *Chem. and Ind.*, 1952, 53) reactions of pyridine–boron trichloride with alcohols in the presence of pyridine were described. Further experiments have now been carried out on the reactions in the absence of pyridine, and the alcohols studied were *n*- and *tert.*-butanol, octan-1-ol, octan-2-ol, and 1-phenylethanol. The reagents were used in equimolecular proportions and chloroform was the solvent. There was no evolution of hydrogen chloride at 20°, but at reflux temperature the gas was steadily evolved during about 20 hours. The other products depended on the individual alcohol and the time of heating. With *n*-butyl alcohol after 20 hours the trialkyl borate (33%), pyridine–boron trichloride (37·5%), and *n*-butyl dichloroboronite–pyridine (68%) were obtained. The yields refer to reactions (3) and (4). With (+)-1-phenylethanol, on the other hand, after 30 hours (±)-1-chloro-1-phenylethane (81%) and a solid which was apparently pyridine–boron oxychloride (100%) (5) were obtained.

$$\mathrm{ROH + C_5H_5N,BCl_3 \longrightarrow C_5H_5N,BCl_2(OR) + HCl} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

$$\mathrm{3C_5H_5N,BCl_2(OR) \longrightarrow B(OR)_3 + 2C_5H_5N,BCl_3 + C_5H_5N} \quad . \; . \; . \; . \quad (4)$$

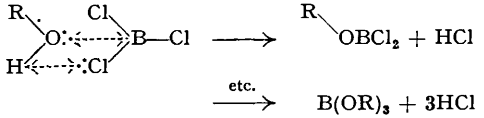
$$\mathrm{ROH + C_5H_5N,BCl_3 \longrightarrow C_5H_5N,BOCl + RCl + HCl} \quad . \; . \; . \; . \; . \; . \quad (5)$$

The existence of boron oxychloride is considered doubtful (Martin, *Chem. Reviews*, 1944, **34**, 461). No inference may be made regarding the loss of optical activity of the alkyl halide, as (±)-1-chloro-1-phenylethane was itself racemised when heated at reflux temperature in chloroform for 7 hours. *tert.*-Butyl alcohol gave results analogous to those with 1-phenylethanol, and the two octyl alcohols gave results intermediate between these and *n*-butyl alcohol. 20 Hours' heating of (±)-octan-2-ol afforded (+)-tri-2-octyl borate (41%) and the (−)-halide (41%), whereas 60 hours' heating gave (−)-2-chloro-octane and no borate. Octan-1-ol after 60 hours afforded a mixture of the borate (87%) and the halide (8%).

These results indicated that the products of reaction (4) on prolonged heating would afford alkyl halide (RCl) and the pyridine–oxychloride complex : $\mathrm{(RO)_3B + 2C_5H_5N,BCl_3 + C_5H_5N \longrightarrow 3RCl + 3C_5H_5N,BOCl}$. This was confirmed for tri-*n*-butyl borate by 45 hours' heating at 150°, *n*-butyl chloride (81%) being collected. A similar experiment using (+)-tri-2-octyl borate yielded the (−)-halide, with some racemisation, and a considerable elimination reaction proceeded simultaneously yielding octene.

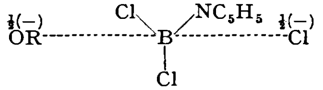
The identity of the *n*-butyl dichloroboronite–pyridine complex (3) was confirmed independently by the addition of pyridine (1 mol.) to the dichloroboronite (1 mol.). It was an oil, and on heating underwent reaction (4); on stronger heating the products reacted further as above. A complex of similar type, *viz.*, the trimethylamine complex of methyl dichloroboronite, from which trimethyl borate could be obtained, was reported by Wiberg and Sütterlin (*Z. anorg. Chem.*, 1935, **222**, 92).

Reactions with pyridine–boron trichloride may now be compared with those of the trichloride itself, and of these, four are now available for such comparison : the hydrolysis, the alcoholysis (1 mol. : 1 mol.), the reaction between trialkyl borates and the chlorinating agent, and the decomposition of chloro-esters. Whereas reactions with boron trichloride are characterised by their great velocity and completeness even at very low temperatures (*e.g.*, −80°), the opposite is the case with the pyridine complex, for prolonged heating is invariably required. The high reactivity of the former reagent is attributed to the " free space" on the boron atom; this is no longer available in the pyridine complex. It is suggested that the first three reactions cited (*i.e.*, replacement of Cl by OH or OR, respectively, and of OR by Cl), which are essentially substitution reactions on the boron atom, are of a nucleophilic type, and a high rate of reaction will be favoured by a low electron density on the boron atom. The replacement of chlorine by hydroxyl or alkoxyl in boron trichloride may be three-centre "end-on" (1) or four-centre "broadside" (6) reactions:



. . . . . . (6)

The mechanism of such a replacement on pyridine–boron trichloride is considered also to be of nucleophilic type, and in view of the completed octet on the boron is pictured as completely analogous to the substitution on an aliphatic carbon atom (Hughes and Ingold; see, *e.g.*, Hughes, *Trans. Faraday Soc.*, 1941, **37**, 603). Thus there are two possibilities, a mechanism analogous to S_N2, involving the transition state (7) or an S_N1 pre-ionisation of the complex (8), and of these the former is preferred, particularly as the complex is insoluble in water. However, the reaction is slow as the somewhat negatively charged boron has a resistance to nucleophilic attack.



. . . . (7)

$$C_5H_5N,BCl_3 \longrightarrow C_5H_5N,\overset{+}{B}Cl_2 + \overset{-}{Cl}$$

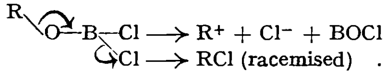
$$C_5H_5N,\overset{+}{B}Cl_2 + ROH \longrightarrow C_5H_5N,BCl_2(OR) + \overset{+}{H} \quad . \; . \; . \; . \; . \; . \quad (8)$$

An alternative explanation of the difference in reactivities between boron trichloride and chloro-esters compared with their pyridine complexes can be deduced from the work of Greenwood, Martin, and Emeléus (*J.*, 1950, 3030; 1951, 1328, 1795, 1915), who showed the ability of boron trifluoride to ionise a neutral oxygen-containing molecule (*e.g.*, water or diethyl ether) to form a complex anion with the negative oxygen fragment [*e.g.*, $C_2H_5^+(BF_3{\cdot}OC_2H_5)^-$; $H^+(BF_3{\cdot}OH)^-$]. If it is assumed that boron trichloride behaves likewise, then transition states in hydrolysis and alcoholysis are $H^+(BCl_3{\cdot}OH)^-$ and $H^+(BCl_3{\cdot}OR)^-$. On the other hand, anions of this type could not be formed in the case of the pyridine complexes for they would each possess a quinquevalent boron atom.

The decomposition of the chloro-esters $RO{\cdot}BCl_2$, and $C_5H_5N,B(OR)Cl_2$ presents a different problem as the products of the two reactions are of different types (4 and 9).

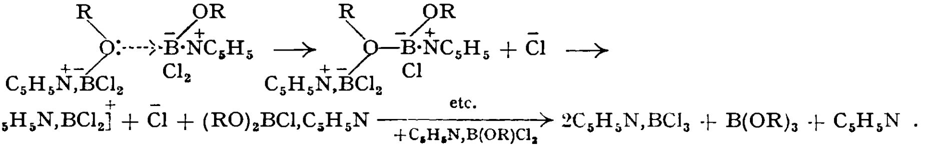
$$3RO{\cdot}BCl_2 \longrightarrow 3RCl + B_2O_3 + BCl_3 \quad . \; . \; . \; . \; . \; . \; . \quad (9)$$

Whatever the mechanism of (9), it is probably of the S_N1 type, as the alkyl chloride in the case of (+)-2-octyl dichloroboronite was obtained racemised (Gerrard and Lappert, *loc. cit.*), and may be as shown in (10). This suggestion requires electron-release from the alkyl



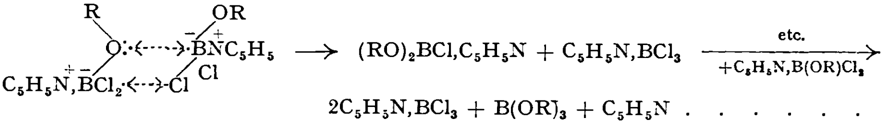
. . . . (10)

group owing to a somewhat positive oxygen atom, and it has been shown that the stability of dichloroboronites is lower the greater the electron-release of the alkyl group. The corresponding pyridine complexes would not have the same tendency, for the electron density on the oxygen atom is not deficient, the boron atom being negatively charged, but

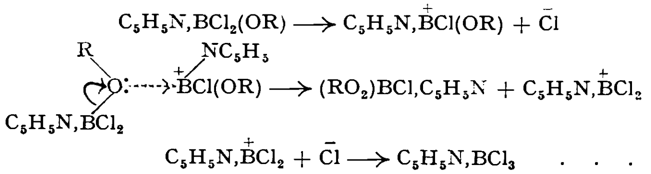


(11)

more likely uses a mechanism analogous to (7) [see (11) or (12)], the borate being obtained with retained configuration. A more likely mechanism may be the S_N1 type (13).



$$(RO)_2BCl,C_5H_5N + C_5H_5N,BCl_3 \xrightarrow[+C_5H_5N,B(OR)Cl_2]{\text{etc.}} 2C_5H_5N,BCl_3 + B(OR)_3 + C_5H_5N \quad (12)$$



$$C_5H_5N,BCl_2(OR) \longrightarrow C_5H_5N,\overset{+}{B}Cl(OR) + \overset{-}{Cl}$$

$$\longrightarrow (RO_2)BCl,C_5H_5N + C_5H_5N,\overset{+}{B}Cl_2$$

$$C_5H_5N,\overset{+}{B}Cl_2 + \overset{-}{Cl} \longrightarrow C_5H_5N,BCl_3 \quad (13)$$

When the pyridine complex was heated more strongly, alkyl chloride was obtained: $C_5H_5N,B(OR)Cl_2 \longrightarrow RCl + C_5H_5N,BOCl$; and here it was completely inverted. This may be due to S_N1 pre-ionisation of the complex, or of pyridine–boron trichloride, chlorine anion then attacking by S_N2 " end-on " mechanism on the carbon atom.

EXPERIMENTAL

Addition of Boron Trichloride (1 *mol.*) *to Alcohols* (3 *mols.*) *in Presence of Pyridine* (3 *mols.*).—The results obtained in these experiments are summarised in Tables 1 and 2, and only the general technique need be described. Boron trichloride (1 mol.) in solvent (15% solution) was slowly (30—60 min.) added to a mixture of the alcohol (0·05—0·10 molar scale, 3 mols.) and pyridine (3 mols.) in solvent (50%), which was cooled to −10° or −80°. In the experiments using *n*-pentane, a mixture of pyridine hydrochloride and pyridine–boron trichloride was precipitated instantly, whereas in chloroform no precipitate formed for both these solids are readily soluble therein. The mixtures were kept for 3 hours at 15—20°. In the chloroform experiments, the solvent was removed at room temperature at 15 mm. and *n*-pentane was added. Both series of experiments were then treated identically. The precipitate was quantitatively filtered off, washed with pentane, placed in a vacuum-desiccator, and weighed. It was then washed with water, and the residue was returned to the desiccator. The water-insoluble solid was pyridine–boron trichloride and the filtrate contained the pyridine hydrochloride. The pentane was removed from the primary filtrate in a vacuum, and the residue (after filtration of the slight precipitate of pyridine hydrochloride which formed on removal of the solvent) was distilled. A small fore-run of unchanged alcohol and pyridine was first obtained, and then the trialkyl borate distilled. In the experiments with *tert.*-butyl alcohol the purification of the trialkyl borate was particularly difficult; hence the crude yields are given in Table 1. To obtain pure specimens two or three further fractionations were required, which lowered the yield to 38% at the best.

Interaction of Alcohols (1 *mol.*) *and Pyridine–Boron Trichloride* (1 *mol.*).—*Octan*-1-*ol.* The alcohol (1·23 g., 1 mol.) and pyridine-boron trichloride (Gerrard and Lappert, *loc. cit.*) (1·90 g., 1 mol.) were refluxed in chloroform (10 c.c.) for 7 days. Hydrogen chloride was continuously evolved. The chloroform was distilled and a pasty white residue remained. This was extracted with successive portions of *n*-pentane. The pentane extract afforded 1-chloro-octane (0·15 g., 8%), b. p. 60—70°/13 mm., n_D^{16} 1·4335, and tri-1-octyl borate (1·10 g., 87%), b. p. 175°/0·5 mm., n_D^{16} 1·4378 (Found: B, 2·8. Calc. for $C_{24}H_{51}O_3B$: B, 2·72%). The pentane-insoluble matter was pasty and was soluble in water.

n-*Butyl alcohol.* The alcohol (3·75 g., 1 mol.) and pyridine–boron trichloride (10·0 g., 1 mol.) in chloroform (15 c.c.) had afforded no hydrogen chloride after 15 hours at 20°. In these experiments effluent hydrogen chloride was absorbed in potassium hydroxide. At reflux temperature the gas (1·66 g., 72%) was evolved in 9 hours, and a further 0·23 g. (10%) was collected after another 11 hours. No boron trichloride was liberated. The mixture on distillation afforded chloroform (12 c.c.), b. p. 62—65°, and a pasty residue which was leached with *n*-pentane, and thereby yielded tri-*n*-butyl borate (1·3 g., 33%), b. p. 105°/8 mm., n_D^{17} 1·4112 (Found: B, 4·83. Calc. for $C_{12}H_{27}O_3B$: B, 4·72%). The remaining solid was washed with water and left pyridine–boron trichloride (2·50 g., 37·5%), m. p. 114°. The aqueous filtrate contained pyridine (2·61 g.), chloride ion (2·24 g.), and boron (0·351 g.). These products were evidently formed by the hydrolysis of *pyridine–*n*-butyl dichloroboronite* (7·5 g., 68%). The latter on hydrolysis would give pyridine (2·54 g.), chloride ion (2·28 g.), and boron (0·349 g.) (as boric acid).

TABLE 1.

	Yields, %, in pentane						Yields, %, in chloroform		
	At −80°			At −10°			At −10°		
R in ROH	$B(OR)_3$	C_5H_5N, HCl	C_5H_5N, BCl_3	$B(OR)_3$	C_5H_5N, HCl	C_5H_5N, BCl_3	$B(OR)_3$	C_5H_5N, HCl	C_5H_5N, BCl_3
Bu^n	76	89·5	10·5	74	87	12·9	88	91	9·1
Bu^i	69	80·1	19·9	72	81	19·2	93	99	1·0
Bu^s	65	75·6	24·3	70	92·8	7·0	92	96	4·1
Bu^t	50 *	74	26·2	69 *	92·5	7·4	71 *	98	1·8
1-Octyl ...	—	—	—	77	84	16	90	98	2·8
2-Octyl †	—	—	—	64	79·5	20·5	84	91·8	8·2
CHPhMe †	—	—	—	69 (RCl, 21%)	—	—	86	93	7·0

* Crude yield. † Gerrard and Lappert (*loc. cit.*).

1-*Phenylethanol.* The alcohol (5·1 g., 1 mol.; α_D^{20} +24·1°) and pyridine–boron trichloride (8·22 g., 1 mol.) were mixed with chloroform (25 c.c.) at 20°. No heat was developed on mixing nor was any hydrogen chloride evolved. After the mixture had been refluxing for 10 hours, 1·17 g. of hydrogen chloride had been evolved; and further quantities of 0·380 g. and 0·0285 g. had been evolved after two further periods of 10 hours each (*i.e.*, total HCl, 1·58 g. Calc.: 1·55 g.). The chloroform was removed in a vacuum; a pasty solid remained, which was extracted with four successive portions (15 c.c. each) of *n*-pentane. The pentane extract on distillation gave (±)-1-chloro-1-phenylethane (4·90 g., 81%), b. p. 80°/15 mm., n_D^{19} 1·5284, α_D^{20} 0° (Found: Cl, 24·9. Calc. for C_8H_9Cl: Cl, 25·3%). The residue (6·07 g.) after pentane extraction was a pasty solid, which appeared to be *pyridine–boron oxychloride* (Calc.: 5·92 g.) (Found: Cl, 25·3; B, 7·4; C_5H_5N, 54·1. C_5H_5ONClB requires Cl, 25·1; B, 7·65; C_5H_5N, 55·8%). It was readily hydrolysed by water. (Yields in this experiment are based on: $ROH + C_5H_5N,BCl_3 \longrightarrow C_5H_5N,BOCl + RCl + HCl$.) (+)-1-Chloro-1-phenylethane (1·97 g., α_D^{20} +34·2°) was heated in chloroform (10 c.c.) for 7 hours at reflux temperature. The solvent was removed in a vacuum and (±)-1-chloro-1-phenylethane (1·83 g., α_D^{20} 0°), b. p. 92°/33 mm., n_D^{23} 1·5302 (Found: Cl, 25·2%), was recovered.

TABLE 2.

	In pentane				In chloroform	
	At −80°		At −10°		At −10°	
R in ROH	B. p./mm.	n_D^t	B. p./mm.	n_D^t	B. p./mm.	n_D^t
Bu^n	109°/15	(20°) 1·4108	116—118°/20	(18°) 1·4106	113°/15	(18°) 1·4106
Bu^i	84—86/10	(20) 1·4035	90/14	(20) 1·4037	90/14	(20) 1·4035
Bu^s	79—80/11	(20) 1·3968	81/15	(17) 1·3980	82/15	(17) 1·3989
Bu^t	64/14	(20) 1·3880	66/17	(21) 1·3881	65/16	(20) 1·3885
1-Octyl ...	—	—	174/0·4	(16) 1·4385	173/0·4	(16) 1·4385

The boron analyses of the various borate samples and the chloride analyses of the pyridine hydrochloride specimens obtained from each reaction were all within 1% of the calculated values.

Octan-2-ol. The (+)-alcohol (6·5 g., 1 mol.; α_D^{20} +4·3°) and pyridine–boron trichloride (9·83 g., 1 mol.) were dissolved in chloroform (25 c.c.). No hydrogen chloride was evolved after 3 days at 20°, but during 20 hours at reflux temperature the gas (1·89 g. Calc.: 1·85 g.) was evolved. The solvent was removed in a vacuum and the residue was extracted with *n*-pentane. This extract afforded (−)-2-chloro-octane (3·10 g., 41%), b. p. 69°/18 mm., α_D^{20} −14·6°, n_D^{20} 1·4279°, and (+)-tri-2-octyl borate (2·73 g., 41%), b. p. 140°/0·1 mm., α_D^{20} +16·6°, $n_D^{16\cdot5}$ 1·4292° (Found: B, 2·82. Calc. for $C_{24}H_{51}O_3B$: B, 2·72%). Water was added to the pentane-insoluble pasty solid and the mixture was filtered. The residue was pyridine–boron trichloride (1·61 g., 16·4%), m. p. 114°, and the water-soluble portion was probably a mixture of pyridine–2-octyl dichloroboronite and pyridine–boron oxychloride (Found: C_5H_5N, 2·94 g.; Cl, 1·26 g.; B, 0·226 g.). In a duplicate experiment (+)-octan-2-ol (5·96 g., 1 mol.; α_D^{20} +4·3°) and pyridine–boron trichloride (9·0 g., 1 mol.) were heated in chloroform (13 c.c.) at reflux temperature for 70 hours. Hydrogen chloride (1·70 g., 99%) was evolved. Pentane extraction of the chloroform-free residue yielded (−)-2-chloro-octane (5·31 g., 78%), b. p. 63°/16 mm., α_D^{20} −14·5°, n_D^{20} 1·4280 (Found: Cl, 23·4. Calc. for $C_8H_{17}Cl$: Cl, 23·9%). The pentane-insoluble residue contained pyridine–boron trichloride (0·148 g., 1·7%) and apparently crude pyridine–boron oxychloride (Found : C_5H_5N, 3·56 g. ; Cl, 1·65 g. ; B, 0·497 g. Calc. : total C_5H_5N 3·66 g. ; $\frac{1}{3}$Cl, 1·65 g. ; B, 0·502 g. in system).

tert.-*Butyl alcohol.* The alcohol (2·12 g., 1 mol.) and pyridine–boron trichloride (5·62 g., 1 mol.) in chloroform (10 c.c.) were heated for 30 hours under reflux. Evacuation (15 mm.) left a pasty white solid (4·94 g. Calc. for $C_5H_5N,BOCl$: 5·10 g.), which appeared to be pyridine–boron oxychloride (Found : Cl, 24·7 ; B, 7·4 ; C_5H_5N, 55·4%). Pure *tert.*-butyl chloride could not be isolated from the condensate owing to difficulty of fractionation.

Interaction of Trialkyl Borates (1 *mol.*), *Pyridine–Boron Trichloride* (2 *mols.*), *and Pyridine* (1 *mol.*).—*Tri*-n-*butyl borate.* The borate (2·84 g., 1 mol.), pyridine–boron trichloride (4·84 g., 2 mols.), and pyridine (0·971 g., 1 mol.) were heated at 150° in absence of solvent for 45 hours under reflux. On evacuation (15 mm.) of the reaction vessel, *n*-butyl chloride (2·84 g., 81%), b. p. 78—79°, n_D^{20} 1·4028 (Found : Cl, 38·2. Calc. for C_4H_9Cl : Cl, 38·4%), was condensed in a trap at −80° and a hard black residue remained in the flask. Carbonaceous decomposition of this solid took place at 200°/0·05 mm., pyridine being collected in the " Drikold " trap.

Tri-2-octyl borate. The (+)-borate (3·87 g., 1 mol.; α_D^{20} +16·5°; from ROH, α_D^{20} +4·3°), pyridine–boron trichloride (3·73 g., 2 mols.), and pyridine (0·750 g.) were heated in absence of solvent at 150° for 45 hours. Distillation afforded a mixture (3·80 g.) (Found : Cl, 5·5%) of octene (77%) and (−)-2-chloro-octane which on bromination and distillation gave (−)-2-chloro-octane (0·81 g.), b. p. 88°/40 mm., n_D^{20} 1·4284, α_D^{20} −6·8° (Found : Cl, 23·6%), and dibromo-octene (1·70 g.), b. p. 135—140°/30 mm., n_D^{20} 1·4970. The residue (4·36 g.) from the primary distillation was hard and black, owing probably to some decomposition. It was largely soluble in water and contained pyridine (2·22 g.), chloride ion (1·44 g.), and boron (0·266 g.) (as boric acid).

Approximate Rate of Reaction of Pyridine–Boron Trichloride (1 *mol.*), *Pyridine* (2 *mols.*), *and* n-*Butanol* (3 *mols.*).—The results of these experiments are summarised in Table 3. From a solution containing pyridine–boron trichloride (7·50 g., 1 mol.), pyridine (6·03 g., 2 mols.), and *n*-butanol (8·47 g., 3 mols.) in chloroform (100 c.c.) kept at either 25° or 80°, samples (10 c.c.) were withdrawn at arbitrary intervals. The chloroform was rapidly removed at 25°/0·2 mm., and *n*-pentane was added to the residue. The precipitate of pyridine–boron trichloride together with pyridine hydrochloride was filtered off, placed in a vacuum-desiccator, and weighed; it was then washed with water; only the water-insoluble pyridine–boron trichloride remained and this was returned to the desiccator. A chloride estimation was carried out on the aqueous washings.

TABLE 3.

Time (hr.)	Temp.	Reaction, % : * (based on weight of C_5H_5N,BCl_3)	Reaction, % : * (based on weight of C_5H_5N,HCl)	Found : Cl, % (Calc. for C_5H_5N,HCl : Cl, 30·7%)
3	25°	4·1	3·1	30·4
48	25	5·4	5·0	30·5
336	25	9·2	8·7	30·5
0·5	80	27·2	25·7	30·6
1	80	40·0	38·2	30·6
2	80	60·1	58·4	30·3
3	80	73·4	73·6	30·2
4	80	81·4	79·3	30·6

* Based on $C_5H_5N,BCl_3 + 2C_5H_5N + 3C_4H_9{\cdot}OH \longrightarrow B(OC_4H_9)_3 + 3C_5H_5N,HCl$.

Interaction of Pyridine (1 *mol.*) *and* n-*Butyl Dichloroboronite* (1 *mol.*).—Pyridine (2·18 g., 1 mol.) in *n*-pentane (15 c.c.) was added to *n*-butyl dichloroboronite (Gerrard and Lappert, *loc. cit.*) (4·27 g., 1 mol.) also in *n*-pentane (15 c.c.) at −80°. A white precipitate was formed immediately and changed to a yellow oil, immiscible with and denser than pentane, when the mixture was allowed to warm to 20° (30 min.). The oil was separated from the solvent and filtered from a slight remaining precipitate. On evacuation (20 mm.) the oil (5·89 g., 91%) remained and was apparently *pyridine*–n-*butyl dichloroboronite* (Found : Cl, 30·5 ; C_5H_5N, 34·2 ; B, 4·7. $C_9H_{14}ONCl_2B$ requires Cl, 30·4 ; C_5H_5N, 33·8 ; B, 4·62%), which was readily decomposed by water to pyridine, hydrogen chloride, and boric acid.

Action of Heat on Pyridine–n-*Butyl Dichloroboronite.*—A sample of the complex (5·00 g.) was heated at 100° for 1 hour. Water was added and the water-insoluble pyridine–boron trichloride (0·660 g., 13·2%) was filtered off. [Yield is based on : $3C_5H_5N,Cl_2BOR \longrightarrow$

$B(OR)_3 + 2C_5H_5N,BCl_3 + C_5H_5N$.] In a separate experiment distillation of the complex (4·90 g.) was attempted and the distillate consisted of two layers; the upper on filtration and distillation afforded tri-*n*-butyl borate (1·4 g., 97%), b. p. 64°/0·5 mm., n_D^{14} 1·4125 (Found: B, 4·9. Calc. for $C_{12}H_{27}O_3B$: B, 4·7%), and the lower gave pyridine–boron trichloride (2·0 g., 80%), b. p. 170°/0·4 mm., m. p. 114°.

When the complex (8·02 g.) was heated at 150° for 45 hours under reflux, and the mixture cooled, a hard black solid separated, covered by a supernatant clear liquid, which on being decanted and distilled afforded *n*-butyl chloride (2·70 g., 84%), b. p. 78—79°, n_D^{14} 1·4007 (Found: Cl, 38·0. Calc. for C_4H_9Cl: Cl, 38·4%). The black solid (5·02 g. Calc. for $C_5H_5N,BOCl$: 4·84 g.) was completely water-soluble, except for a slight black tar, and appeared to be crude pyridine–boron oxychloride (Found: C_5H_5N, 53·2; Cl, 26·7; B, 7·6%).

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