567. *Interaction of Alcohols and Boron Trichloride.*

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The borate, chloroboronate $BCl(OR)_2$, and dichloroboronite $BCl_2{\cdot}OR$, respectively, were rapidly obtained when the appropriate alcohol (*n*-, *iso*-, and *sec*.-butyl, respectively; 3, 2, and 1 mol. for each alcohol) was mixed with boron trichloride (1 mol.) at low temperature. It is suggested that these products are formed by the broadside 4-centre approaches of reactants. The chloroboronates readily decomposed at room temperature affording the alkyl chloride, the trialkyl borate, and boron trioxide, but the dichloroboronites decomposed much less readily and then gave alkyl chloride, boron trichloride, and boron trioxide. Probable mechanisms are discussed. Proportionation readily occurred between the trichloride and trialkyl borate, the chloro-esters being formed.

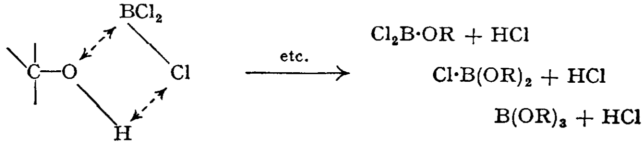
Rearrangement to *tert*.-butyl chloride occurred in the decomposition of the *iso*butyl chloro-esters; and *tert*.-butyl alcohol (3 mols.) rapidly gave *tert*.-butyl chloride (3 mols.) and boric acid (1 mol.) when mixed with boron trichloride (1 mol.). Dealkylation of tributyl borates (except *tert*.) by hydrogen chloride was not observed. Even hydrogen bromide reacted but slowly.

IN a previous paper (*J*., 1951, 1020) we described experiments on the alcohol–, the alcohol–pyridine–, and the ether–boron trichloride systems with special reference to optically active octan-2-ol and 1-phenylethanol, which were considered as useful standards with respect, not only to the degree of reactivity of the alcoholic carbon atom, but also to the steric course. The function of pyridine was explained, and the preparation of a number of trialkyl borates by means of monopyridinoboron trichloride will be described elsewhere. Extending our observations to mixed ethers of the type of *n*-butyl *sec*.-butyl ether, we found it necessary to have precise information on the related alkyl dichloroboronites $BCl_2{\cdot}OR$, and dialkyl chloroboronates $BCl(OR)_2$.

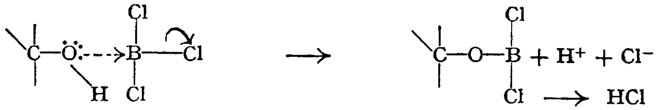
Apart from work by Wiberg and Sütterlin (*Z. anorg. Chem.*, 1931, **202**, 1, 22, 31), which concerned only methyl and ethyl compounds, manipulated in an enclosed, low-pressure apparatus, and an observation on di*iso*amyl chloroboronate by Kinney, Thompson, and Cheney (*J. Amer. Chem. Soc.*, 1935, **57**, 2396), no information was available to us. We therefore turned to the interaction of the isomeric butyl alcohols with boron trichloride and, although we can now see the need for most detailed and protracted study, we feel it desirable to submit results obtained so far, because of the interest now being shown in esters containing boron (Cook, Ilett, Saunders, and Stacey, *J*., 1950, 3125) and in the interaction of ethyl alcohol with such chlorides as zirconium tetrachloride (with correlation to the silicon tetrachloride system) (Bradley, Abd-el Halim, and Wardlaw, *J*., 1951, 280; cf. *Chem. and Ind.*, 1951, 310, and Gerrard, *ibid*., p. 463).

Addition of boron trichloride (1 mol.) to *n*-, *iso*-, and *sec*.-butyl alcohol (3 mols.) in pentane readily afforded the corresponding trialkyl borate, unaccompanied by alkyl chloride. We suggest that the stepwise dechlorination proceeds by a four-centre broadside approach (1) rather than by a type of three-centre end-on approach (2):

(1)



(2)



The dechlorination proceeds quickly even at low temperatures, and neither of the intermediate chloro-esters nor the trialkyl borate undergoes dealkylation by hydrogen chloride under the prevailing experimental conditions. Against the inclination to formulate the mechanism as a two-stage one entailing the formation of an addition compound $\overset{R}{\underset{H}{>}}O{:}BCl_3$, followed by decomposition, either by direct expulsion of hydrogen chloride (1) or by extrusion of a proton and a chlorine anion (2), one must consider our observation (*loc. cit.*) that in the co-ordination compound $C_5H_5N{:}BCl_3$, the chlorine atoms have much lower reactivity than in the trichloride itself.

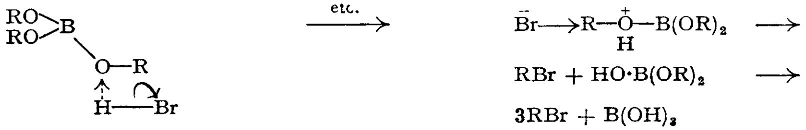
Addition of the trichloride (1 mol.) to *tert.*-butyl alcohol (3 mols.) afforded only *tert.*-butyl chloride and boric acid in excellent yield. Here the very reactive alcoholic carbon atom is dominating the situation, and, gleaning information from the 1-phenylethanol example (*loc. cit.*), we suppose a primary formation of some molecules of dichloroboronite, which undergo a S_{N}i (Hughes and Ingold) type of decomposition to alkyl halide and BOCl, whereas the latter and hydrogen chloride could react with the alcohol on their own account. Probably a $S_{\mathrm{N}}1$ mechanism proceeds too; for some loss in optical activity occurred in the 1-phenylethyl system. From experience with the phosphorus trichloride system (Gerrard, *J.*, 1940, 1464; 1944, 85), we suggest the rather unconventional process of a rapid dechlorination to the trialkyl borate, followed by a rapid dealkylation of that by means of hydrogen chloride. The experimental result, however, shows that, in attempting to generalise about an alcohol–non-metallic inorganic halide system from observations with ethanol, one should have regard to the degree of reactivity of the alcoholic carbon atom.

n-Butyl dichloroboronite, $BCl_2{\cdot}OR$, was readily formed in excellent yield by adding the alcohol (1 mol.) to the trichloride (1 mol.). It slowly decomposed at 15°; but there was 81% decomposition in 15·5 hours at 100°, the products being *n*-butyl chloride, boron trichloride, and boron trioxide, indicating an overall equation: $3BuO{\cdot}BCl_2 \longrightarrow 3BuCl + BCl_3 + B_2O_3$. Wiberg and Sütterlin (*loc. cit.*) suggested the intermediate formation of the oxychloride, BOCl, which disproportionated thus: $3BOCl \longrightarrow BCl_3 + B_2O_3$. Having regard to the steric course in the (+)-2-octyl system, in which the alkyl chloride was involved in preponderant inversion plus considerable racemisation, it would appear that the mechanism is not merely the $S_{\mathrm{N}}2$ one: $RO{\cdot}BCl_2 \longrightarrow Cl^- \dashrightarrow RO{\cdot}BCl^+ \longrightarrow RCl + BOCl$. The $S_{\mathrm{N}}1$ mechanism $RO{\cdot}BCl_2 \longrightarrow R^+ + BOCl_2^- \longrightarrow R^+ + Cl^- + BOCl \longrightarrow RCl$ probably operates as well, and may even be accompanied by the intramolecular S_{N}i mechanism. In a similar way, *iso*butyl dichloroboronite was obtained, and at 100° this decomposed to the extent of 62% in 24 hours; but considerable rearrangement to *tert.*-butyl chloride had occurred. This indicates a hydrogen atom transfer consequent on a $S_{\mathrm{N}}1$ process. Definite evidence for the formation of *sec.*-butyl dichloroboronite at −80° was secured; but 5 minutes after the cooling-bath had been removed, gelation began, and after 30 minutes decomposition to *sec.*-butyl chloride, boron trichloride, and boron trioxide was well advanced.

Di-*n*-butyl chloroboronate was formed from the alcohol (2 mols.) and trichloride (1 mol.) at −80°; but decomposition to alkyl chloride, trialkyl borate, and boron trioxide readily occurred at 20°, and the overall equation indicated is $3BCl(OR)_2 \longrightarrow 3RCl + B(OR)_3 + B_2O_3$. Di*iso*butyl chloroboronate was formed under similar conditions, and it readily decomposed at 0° giving alkyl (mainly *tert.*-butyl) chloride, tri*iso*butyl borate, and boron trioxide. Evidence for the formation at −80° of di-*sec.*-butyl chloroboronate was similarly secured. It decomposed to *sec.*-butyl chloride, tri-*sec.*-butyl borate, and boron trioxide.

The chloro-esters were readily formed at low temperatures by interaction of the trichloride and trialkyl borate. Results of dealkylation of the tri-esters by means of hydrogen halides are recorded in Table III. Having regard to the steric course in the case of the 2-octyl ester, we suggest the mechanism (3). Except with tri-*tert.*-butyl borate (rapid dealkylation),

(3)



dealkylation by means of hydrogen chloride was not observed. Attack by hydrogen bromide was slow, but that by hydrogen iodide was much quicker. In contrast with the phosphorous ester–hydrogen halide system, the second and the third dealkylation must have followed the first quickly, because there was no sign of any of the intermediate dealkylated forms.

Data described herein are now available for comparison with those for the phosphorus trichloride–alcohol (Gerrard, *loc. cit.*) and the silicon tetrachloride–alcohol (Gerrard and Woodhead, *J.*, 1951, 519) system.

EXPERIMENTAL.

(Percentage yields are based on the equations stated.)

Trialkyl Borates from Alcohol (3 *mols.*) *and Boron Trichloride* (1 *mol.*).—The trichloride in pentane solution was added to the alcohol in pentane at −10°. After the mixture had been kept for 30 minutes at 15°, all volatile matter was removed at 15 mm., the residue then being weighed and distilled. Results are recorded in the following Table, the borates being characterised by comparison with the completely analysed specimens obtained in a previous investigation (Gerrard and Lappert, *loc. cit.*).

Butyl alcohol.	Weight, g.	BCl_3, g.	Total vol. of pentane, c.c.	Residue, g.	B.p./mm.	*n*.	Distilled $B(OR)_3$, g.	Boron, %, found.*
n-	3·78	2·0	15	3·87	110°/11	n_D^{17} 1·4118	3·6 (92%)	4·84
iso-	8·9	4·7	30	9·17	96°/12	n_D^{18} 1·4050	8·55 (93%)	4·90
sec.-	10·4	5·4	35	11·2	83°/14	n_D^{19} 1·3974	8·6 (80%) (Repeat, 89%)	4·83

* Calc. for $B(OC_4H_9)_3$: B, 4·70%.

Addition of the trichloride (5·4 g., 1 mol.; in pentane, 10 c.c.) to *tert.*-butyl alcohol (10·4 g.) in pentane (25 c.c.) at −10° caused immediate development of a white precipitate, and there was scarcely any evolution of hydrogen chloride. After the reaction mixture had been kept at 15° for 15 minutes volatile matter was removed at 15 mm. From the solid residue (3·4 g.) a liquid (0·45 g.), b. p. 30—40°/40 mm. (free from boron), probably the alcohol, was obtained, and the final residue appeared to be essentially boric acid (2·8 g., 97% based on the reaction : $BCl_3 + 3ROH \longrightarrow 3RCl + H_3BO_3$). There was no evidence of the formation of tri-*tert.*-butyl borate. The operation then being conducted in xylene (total volume 15 c.c.), in order to isolate *tert.*-butyl chloride, the trichloride (3·6 g.) and alcohol (6·74 g.) afforded a brown gel which changed into a white spongy precipitate overnight. From the mixture, *tert.*-butyl chloride (7·6 g., 90%), b. p. 50—53°, n_D^{18} 1·3872, d_4^{17} 0·832 (Found : Cl, 37·9. Calc. for C_4H_9Cl : Cl, 38·4%), was obtained. In the aqueous washing of the residue, boric acid (1·8 g., 95%) was found.

Interaction of Butyl Alcohols (1 *mol.*) *and Boron Trichloride* (1 *mol.*).—Dropwise addition (1·25 hours) of *n*-butyl alcohol (4·78 g.) in pentane (8 c.c.) to the trichloride (6·0 g.) in pentane (15 c.c.) at −10° caused a vigorous and constant evolution of gas. After 12 hours the mixture was distilled. Boron trichloride distilled constantly with the pentane, and finally *n*-butyl chloride (2·3 g.), b. p. 77—78°, n_D^{19} 1·4030, and a residue (1·4 g.) which contained boron trioxide (0·91 g., by titration) were obtained. In this and later cases, further evidence of the presence of boron trioxide was the hygroscopic nature of the residue, and the evolution of heat on addition of water.

In the absence of solvent, *n*-butyl alcohol (7·0 g.) was added to the trichloride (11·2 g.) at −80°, the outlet of the reaction vessel being attached to absorption tubes containing potassium hydroxide kept at 0°. The reaction vessel was then mechanically shaken for 1·5 hours at 15°; by this time, the absorption tubes contained boron and chlorine equivalent to 3·15 g. of hydrogen chloride (representing 30·5% of total chlorine in the system) and boron trichloride (0·3 g.). n-*Butyl dichloroboronite* remained in the vessel as a colourless liquid (14·7 g., 100%) (Found : Cl, 45·5; B, 7·1%); on distillation, it had b. p. 42°/20 mm. (Found : Cl, 45·6; B, 7·0. $C_4H_9OCl_2B$ requires Cl, 45·8; B, 7·02%). It (5·0 g.) was readily hydrolysed with water to *n*-butyl alcohol (1·82 g., 76%), b. p. 114—115°, n_D^{16} 1·4008.

Addition of *iso*butyl alcohol (5·3 g.) in pentane (10 c.c.) to the trichloride (8·4 g.) in pentane (15 c.c.) at −10°, followed by shaking (30 minutes) and evaporation at 40 mm., gave a residue (11·3 g., 100%) which was mainly iso*butyl dichloroboronite* (Found : Cl, 43·2; B, 7·1%), b. p. 34°/20 mm., n_D^{18} 1·4099, d_4^{20} 1·047 (Found : Cl, 45·3; B, 6·92%).

sec.-Butyl alcohol (4·85 g.) was added to the trichloride (7·7 g., 1 mol.) at −80° as described for *n*-butyl alcohol. Boric acid was not precipitated, but gelation occurred within 5 minutes of removal of the cooling-bath, and after 30 minutes the residue (8·38 g.) was a white spongy mass. Analysis of the absorption-tube contents showed that hydrogen chloride (2·6 g., 36% of total chlorine present) and boron trichloride (1·25 g.) had been absorbed. At 15°/0·5 mm. a liquid (5·4 g.) passed from the reaction residue into a trap at −80°, and the final residue (2·48 g.) contained boron trioxide (1·7 g. by titration). The distillate (5·4 g.) contained boron and ionisable chlorine equivalent to 0·53 g. of boron trichloride, and after being washed and dried afforded *sec.*-butyl chloride (4·4 g., 73%), b. p. 68°, n_D^{20} 1·3974. To determine whether the dichloroboronite is formed, the reagents (ROH, 1·70 g.; BCl_3, 2·70 g.) were mixed at −80°, and dry nitrogen was passed through the mixture for 15 minutes at −80°. Only hydrogen chloride (0·79 g., 94%) was absorbed in the tube. The residue was immediately hydrolysed in an enclosed system, and from the analysis (Found: Cl, 45·0; B, 6·8%) it appeared that the dichloroboronite had been formed at −80°.

Approximate Rate of Decomposition of n-*Butyl Dichloroboronite*.—As *n*-butyl dichloroboronite tends to undergo decomposition to alkyl chloride, boron trioxide, and boron trichloride, a preliminary investigation was made to define the practical limits of stability. Boron trichloride evolved from the dichloroboronite at 15° and at 100° was measured at specified time intervals. *n*-Butyl dichloroboronite (8·3 g.) (Found: Cl, 45·5; B, 7·1%) was put into a flask fitted with an upright, water-cooled condenser, the outlet of which was connected to an absorption tube containing potassium hydroxide. After 44 hours at 15°, the absorption tube was changed, and by this time 0·032 mol. of boron trichloride had been evolved for 3 mols. of dichloroboronite. The vessel was then kept at 100° for 15·5 hours, and the absorption tube changed at specified time intervals. Results are recorded below:

Time, hours	1·25	2·25	3·5	4·5	6·5	7·9	10·9	15·5
BCl_3, g.	0·139	0·621	1·00	1·23	1·43	1·51	1·54	1·67
BCl_3, mol. per 3 mols. of BCl_2·OBu	0·0657	0·299	0·467	0·648	0·692	0·740	0·763	0·805

Other signs of reaction were the increasing amount of precipitate, and increasing rate of reflux. After 15·5 hours the amount of trichloride evolved corresponded to 81% of the amount required for the reaction $3BCl_2·OBu \longrightarrow 3BuCl + BCl_3 + B_2O_3$, and the residue on distillation afforded a liquid, b. p. 72—74°, mainly *n*-butyl chloride but containing boron trichloride (10·7%). After being washed and dried, the distillate gave *n*-butyl chloride (4·0 g., 81%), b. p. 76—77°, n_D^{19} 1·4022. The residue (1·5 g.) from the primary distillation contained boron trioxide (1·19 g., 96% by titration).

Decomposition of iso*Butyl Dichloroboronite*.—This dichloroboronite (8·3 g.) was heated at 100° as described for the *n*-butyl compound. Results are recorded in the Table below. On distillation, a liquid (4·5 g.), b. p. 45—65°, and a residue of white powder (1·6 g.) were obtained. The distillate contained dissolved hydrogen chloride and boron trichloride, and these were removed by means of moist lead carbonate. The final liquid had a wide distillation range and was a mixture of *tert.*- and *iso*-butyl chlorides (3·9 g., 79%), b. p. 50—68°, separated into fractions, (i) b. p. 50—53° (1·2 g.), n_D^{16} 1·3900 (Found: *tert.*-butyl chloride, 87%), (ii) b. p. 53—64° (2·4 g.), n_D^{17} 1·3930 (Found: *tert.*-BuCl, 55%), and (iii) b. p. 64—68° (0·3 g.), n_D^{17} 1·3962 (Found: *tert.*-BuCl, 17%). The proportion of the tertiary chloride was determined by means of cold alcoholic potassium hydroxide. Even after being in a similar solution of alcoholic potassium hydroxide for 72 hours, a specimen of *iso*butyl chloride gave only 2·2% of Cl (Calc.: Cl, 38·4%). The residue (1·6 g.) from the primary distillation contained boron trioxide (1·2 g., 97%) as indicated by treatment with water and subsequent titration.

Time, hours	1	2·1	3·2	4·2	5·2	6·1	7·1	8·4	9·4	12·6	15·9	20·7	24·2
BCl_3, g.	0·126	0·147	0·175	0·228	0·433	0·629	0·750	0·813	0·862	0·954	1·037	1·192	1·298
BCl_3, mol. per 3 mols. of BCl_2·OR	0·06	0·07	0·08	0·11	0·21	0·30	0·36	0·39	0·414	0·46	0·50	0·52	0·62

Interaction of n-*Butyl Dichloroboronite and* n-*Butyl Alcohol*.—The alcohol (4·12 g., 1 mol.) was added to the dichloroboronite (8·6 g., 1 mol.) at −80°, effluent gases being trapped as described before. After the apparatus had been at 15° for 18 hours, it was found that hydrogen chloride (1·86 g., 92% based on replacement of one chlorine atom) had been evolved. At 15°/15 mm. volatile matter was removed from the residue (10·7 g.); from the final residue (5·5 g.), tri-*n*-butyl borate (3·95 g., 93%, based on decomposition of the chloroboronate), b. p. 70—80°/0·2 mm. (redistilled, b. p. 119°/18 mm.), n_D^{18} 1·4110 (Found: B, 4·8. Calc.: B, 4·7%), was obtained. The final distillation residue (from the 0·2-mm. distillation) contained boron trioxide (1·33 g., 100% based on decomposition). At 15 mm. the loss in weight was 5·2 g., and the calculated loss, if due to *n*-butyl chloride, from decomposition is 5·1 g. It would appear that the monochloroboronate, $BCl(OR)_2$, is formed, but that it decomposes at room temperature according to $3BCl(OR)_2 \longrightarrow 3RCl + B(OR)_3 + B_2O_3$.

Di-n-*Butyl Chloroboronate*.—Addition (1 hour) of the alcohol (18·6 g., 2 mols.) to the trichloride (14·8 g., 1 mol.) at −80°, followed by mechanical shaking at 0° for 35 minutes, led to a loss in weight of 9·4 g. [Calc. for hydrogen chloride from $2ROH + BCl_3 \longrightarrow BCl(OR)_2 + 2HCl$: 9·2 g.]. There can be little doubt that the residue was a good specimen of *di*-n-*butyl chloroboronate*, n_D^{20} 1·4132 (Found: Cl, 17·7; B, 5·9. $C_8H_{18}O_2ClB$ requires Cl, 18·4; B, 5·65%). To follow the approximate rate of decomposition at 20°, another specimen (16·85 g.), n_D^{20} 1·4141, d_4^{20} 0·941 (Found: Cl, 18·1; B, 5·5%), was prepared and samples were withdrawn from it at intervals during 6 hours in order to determine readily (water) hydrolysable chlorine and boron. The chlorine value fell continuously as shown below, whereas the boron values were, 5·5, 5·7, 5·7, 5·7, 5·7, 5·7, and finally 5·8%.

Time, hours	1·25	2·33	3·60	4·80	5·33	63
Hydrolysable Cl, %	13·8	12·0	9·8	7·3	6·9	0·88
Extent of decomp., %	25	35	47	61	63	95

The final mixture (13·85 g.) was heated under reflux for 2 hours and distilled. *n*-Butyl chloride (5·45 g., 83%), b. p. 76—80°, tri-*n*-butyl borate (4·9 g., 89%), b. p. 80—100°/0·4 mm., and a residue (3·0 g.) which contained boron trioxide (1·65 g., 98%) were obtained. The triester was redistilled, b. p. 108°/10 mm., n_D^{20} 1·4105 (Found : B, 4·8. Calc. : B, 4·7%). After being treated with lead carbonate, the alkyl chloride was redistilled : (i) b. p. 76—76·5/765 mm. (1·2 g.), n_D^{17} 1·4038, d_4^{20} 0·877; (ii) b. p. 76·5—77°/765 mm. (1·8 g.), n_D^{17} 1·4042, d_4^{20} 0·879; (iii) b. p. 77—79°/765 mm. (1·8 g.), n_D^{17} 1·4048, d_4^{20} 0·880.

Interaction of iso*Butyl Alcohol* (2 *mols.*) *and Boron Trichloride* (1 *mol.*).—The alcohol (7·5 g.) was added (35 minutes) to the trichloride (6·0 g.) at −80°, and the mixture kept for 15 minutes with the cooling-bath removed. The residue (10·03 g.; loss in weight, 3·47 g.) (Found : Cl, 20·2; B, 5·9%) was probably mainly the chloroboronate—the loss in weight due to hydrogen chloride evolution should be 3·70 g.

Boron Trichloride (1 *mol.*) *and* sec.*-Butyl Alcohol* (2 *mols.*).—The alcohol (7·6 g.) was added (1 hour) to the trichloride (6·0 g.) at −10°, an absorption tube being attached to the vessel. The latter was then shaken at 15° for 30 minutes; the tube had then absorbed hydrogen chloride (3·1 g., 83%) and boron trichloride (0·5 g., based on titration). On distillation, the residue (10·0 g.) afforded crude *sec.*-butyl chloride (4·25 g., 90%), b. p. 60—70°, b. p. 68°, n_D^{10} 1·4012 (after treatment with lead carbonate), and tri-*sec.*-butyl borate (3·0 g., 76%), b. p. 90—91°/20 mm., n_D^{19} 1·4018 (Found : B, 4·7. Calc. : B, 4·7%), and a residue of boron trioxide (1·34 g., 100%, by titration).

When the alcohol (2·2 g.) was added (15 minutes) to the trichloride (1·75 g.) at −80°, and then nitrogen passed through the mixture for 10 minutes, hydrogen chloride (1·00 g., 94%) was absorbed in the tube attached; the residue was then immediately hydrolysed (Found : Cl, 18·4; B, 5·3. *Di*-sec.*-butyl chloroboronate*, $C_8H_{18}O_2ClB$, requires Cl, 18·4; B, 5·65%).

*Decomposition of Di*iso*Butyl Chloroboronate.*—This process seemed to involve rearrangement to *tert.*-butyl chloride, and so the titrations to estimate the amounts of readily hydrolysable chlorine were carried out rapidly. Even so, the results must be taken as showing a low limit of the rate. A freshly prepared specimen of the chloroboronate (8·4 g.), n_D^{19} 1·4060, d_4^{20} 0·938 (Found : Cl, 18·4; B, 5·6%), was kept at 0° whilst samples were removed for analysis. The approximate rate of decomposition is indicated below :

Time, hours	0	0·43	0·67	1·43	2·84	18·0
Readily hydrolysable Cl, %	14·3	7·7	6·5	6·5	5·8	3·7
Decomposition, %	22	58	65	65	68·5	80

The remaining liquid (5·25 g.) afforded a mixture of *tert.*- and *iso*-butyl chloride (2·15 g., 86%), b. p. 50—58°, tri*iso*butyl borate (2·0 g., 95%), b. p. 67°/0·5 mm., n_D^{20} 1·4035 (Found : B, 4·8. Calc. : B, 4·7%), and a residue (0·85 g.) containing boron trioxide (0·63 g., 99%). The mixed chlorides gave fractions of b. p. 52—53° (0·8 g.), n_D^{15} 1·3899 (Found : Bu^{t}Cl, 94%), b. p. 53—55° (0·8 g.), n_D^{15} 1·3900 (Found : Bu^{t}Cl, 89%), and b. p. 55—57° (0·26 g.), n_D^{15} 1·3908 (Found : Bu^{t}Cl, 87%), the *tert.*-butyl chloride being determined by hydrolysis in cold 3N-nitric acid followed by titration of the chloride by Volhard's method. A specimen of *iso*butyl chloride was mixed with a similar dilute solution of nitric acid and set aside for 72 hours (Found : Cl, 2·4. Calc. : Cl, 38·4%).

Interaction of Boron Trichloride and Trialkyl Borates.—Tri-*n*-butyl borate (1·88 g., 1 mol.) was added to the trichloride (1·85 g., 2 mols.) at −80°. The product was shaken at 18° for 15 minutes, and then at 18°/15 mm. for 10 minutes. The final residue (3·73 g., 100%) had n_D^{20} 1·4162, d_4^{20} 1·079 (Found : Cl, 44·2; B, 6·85. Calc. for the dichloroboronite, $C_4H_9OCl_2B$: Cl, 45·8; B, 7·0%). It had b. p. 38—40°/20 mm. (constant) and left no residue.

Similarly, tri*iso*butyl borate (1·15 g., 1 mol.) and the trichloride (1·9 g., 2 mols.) afforded a residue (Found : Cl, 44·0; B, 6·8%), which distilled constantly at 36°/20 mm. and left no residue.

From tri-*n*-butyl borate (14·4 g., 2 mols.) and trichloride (3·7 g., 1 mol.) at −80°, the final residue, after being kept at −10°/15 mm. for 15 minutes (18·1 g., 100%), had n_D^{20} 1·4141, d_4^{20} 0·941 (Found : Cl, 18·1; B, 5·15. Calc. for the chloroboronate, $C_8H_{18}O_2ClB$: Cl, 18·4; B, 5·65%). This material decomposed readily as already shown. Similarly tri*iso*butyl borate (6·7 g., 2 mols.) and trichloride (1·7 g., 1 mol.) were mixed at −80°, and thoroughly shaken at −10°/15 mm. for 5 minutes. The resulting chloroboronate (8·3 g., 98%) had n_D^{19} 1·4060, d_4^{20} 0·938 (Found : Cl, 18·4; B, 5·6%), and readily decomposed as shown.

Tri-*sec.*-butyl borate (1·8 g., 1 mol.) was added to boron trichloride (1·8 g., 2 mols.) at −80°. The outlet of the reaction vessel was connected to an absorption tube containing potassium hydroxide. The cooling-bath was then removed, and the mixture allowed to warm to 20°; within 5 minutes a white gel developed and boron trichloride was evolved. The vessel was kept at 20° for 15 hours, boron trichloride (0·62 g.) being collected in the absorption tube. The remainder (3·0 g.) afforded *sec.*-butyl chloride (2·2 g.), b. p. 67—69°, contaminated with boron trichloride and, after treatment with moist lead carbonate, redistillation gave *sec.*-butyl chloride (1·9 g.), b. p. 67·5—68·5°, n_D^{15} 1·4008. The residue (0·74 g.) of the primary distillation contained boron trioxide (0·48 g., 90% based on boron in the system).

Tri-*tert.*-butyl borate (2·62 g., 1 mol.) and the trichloride (1·56 g., 1 mol.) at −80° afforded boron trioxide (0·762 g., 96%) and *tert.*-butyl chloride (2·95 g.), b. p. 50—53°, n_D^{19} 1·3878 (Found : Cl, 38·0. Calc. for C_4H_9Cl : Cl, 38·4%).

Dealkylation by Hydrogen Halides.—Results of the passage of hydrogen halides through the trialkyl borates are recorded below. From *tert.*-butyl borate, there were immediate formation of boric acid and evolution of heat. The *tert.*-butyl chloride (2·7 g., 94%), b. p. 52°, was shaken with lead carbonate to remove dissolved hydrogen chloride, and the pure chloride (2·4 g.) then had b. p. 51°, n_D^{20} 1·3862

							Borate recovered :			
No.	Butyl borate.	Weight, g.	HX.	Time of passage, hours.	Temp.	Yield of RX, g. (and b. p.).	g.	b. p. (mm.).	n_D.	Found : B, %.
1	*n*-	9·1	HCl	8	35°	none	9·0	112°/12	1·4107 (20°)	4·7
2	*sec*.-	5·1	HCl	12 30	120 15	none	4·9	84°/15	1·3968 (20°)	4·8
3	*iso*-	2·54	HCl	13 30	115 20	none	2·24	96°/14	1·4059 (16°)	(no residue)
4	*tert*.-	2·38	HCl	$\frac{1}{2}$	15	2·4 (51°)	(Residue of boric acid, 0·63 g., 98%)			
5	*n*-	5·5	HBr	15	18	none	5·4	116°/18	1·4115 (18°)	—
6	,,	2·25	HBr	7	115	1·4 (97—100°)	1·35	114°/14	1·4111 (20°)	4·7
7	*sec*.-	2·65	HBr	60	20	4·0 (88—90°)	(Residue, 0·8 g. containing boric acid, 0·65 g.)			
8	*iso*-	2·50	HBr	72	20	none	2·42	96°/14	1·4062 (16°)	—
9	,,	3·80	HBr	16 30	115 20	1·7 (86—89°)	2·27	96°/15	1·4042 (21°)	—
10	*n*-	5·7	HI	$\frac{3}{4}$	18	1·0 (43°/18 mm.)	4·7	114°/18	1·4108 (20°)	—
11	,,	5·5	HI	4	50	12·7 (130°) *	—	—	—	—
12	*sec*.-	1·8	HI	2	20	2·4 (117—119°)	(Residue containing boric acid, 0·46 g., 96%)			

* Found : I, 69·6. Calc. for C_4H_9I : I, 69·1%.

(Found : Cl, 38·3. Calc. for C_4H_9Cl : Cl, 38·4%). The alkyl bromide in expt. 6 was shaken with lead carbonate, and it then had b. p. 99—100°, n_D^{20} 1·4361. In expt. 9 the alkyl bromide was shaken with lead carbonate before redistillation; it had n_D^{23} 1·4328. There was a primary residue (0·30 g.) of boric acid. In expt. 12, primary distillation afforded a liquid, b. p. 105—120°, and a residue of boric acid (0·46 g., 96%). The liquid was shaken with solid sodium thiosulphate and then redistilled; it had b. p. 117—119°, n_D^{20} 1·4945. Tri*iso*butyl borate (2·65 g.) and hydrogen iodide (12 hours at 20°) afforded unchanged borate (1·32 g., 50%), b. p. 96—97°/14 mm., n_D^{16} 1·4061, but the other material was not identified with certainty.

One of us (M. F. L.) thanks the D.S.I.R. for a personal grant.

THE NORTHERN POLYTECHNIC, HOLLOWAY ROAD, N.7.

[*Received, June 4th*, 1951.]