Reactions in Boron Trifluoride–n-*Butyl Alcohol–Tri*-n-*butyl Borate Systems.*

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[Reprint Order No. 5641.]

n-Butyl difluoroboronite, BuO·BF_2, was obtained by action of boron trifluoride on tri-*n*-butyl borate, the reaction being reversible at high temperatures. Di-*n*-butyl fluoroboronate, $(BuO)_2BF$, could not be isolated by reaction of boron trifluoride and tri-*n*-butyl borate (2 mols.) or from the latter and the difluoroboronite. The difluoroboronite reacted with pyridine to give pyridine–boron trifluoride and tri-*n*-butyl borate, with solid sodium hydroxide to give *n*-butanol, with water to give a boron trifluoride–di-*n*-butanol complex, BF_3,2BuOH, and boric acid, and with *n*-butanol to give the same complex and a 1 : 1 : 1 compound between boron trifluoride, *n*-butanol, and tri-*n*-butyl borate. These compounds were identified by reaction with water, sodium hydroxide, pyridine, boron trifluoride, and tri-*n*-butyl borate, and by thermal degradation and each also by synthesis. Their structures are discussed.

The original aim of this investigation was to prepare difluoroboronites (RO·BF_2) and fluoroboronates [$(RO)_2BF$] and to compare and contrast methods of preparation and properties of these compounds with the corresponding chlorine analogues. Such fluorine compounds have received scant attention. Gasselin (*Ann. Chim. Phys.*, 1894, **3**, 5) reported the preparation of the methyl esters from sodium methoxide and boron trifluoride, and from boron trifluoride and trimethyl borate. These results are contrary to the findings of Meerwein and Pannwitz (*J. pr. Chem.*, 1934, **141**, 123) who by the former reaction obtained a co-ordination compound BF_3,NaOMe. Goubeau and Lücke (*Annalen*, 1951, **575**, 37) prepared the same methyl esters, by using Gasselin's second method, and deduced from Raman-spectra investigations that the difluoroboronite was dimeric. Similar conclusions had been drawn by Allen and Sugden (*J.*, 1932, 760) from parachor measurements, but methods of preparation were not stated. Goubeau and Lücke (*loc. cit.*) observed that dimethyl fluoroboronate, although having a constant b. p. (52·7°), could not be crystallised on cooling, but instead afforded the difluoroboronite, presumably by disproportionation: $2(MeO)_2BF \longrightarrow (MeO)_3B + MeO\cdot BF_2$. Meerwein, Battenberg, Gold, Pfeil, and Willfang (*J. pr. Chem.*, 1939, **154**, 83) suggested that boron trifluoride formed 1 : 1 and 2 : 1 co-ordination complexes with trialkyl borates and that these were very unstable, tending to disproportionate into difluoroboronites and fluoroboronates. Cook, Ilett, Saunders, and Stacey (*J.*, 1950, 3125) attempted to prepare di-*n*-butyl fluoroboronate by interaction of the boron trifluoride–diethyl ether complex and tri-*n*-butyl borate, but a very unstable compound was obtained, which suggested disproportionation of similar type to that observed by Goubeau and Lücke.

Of the methods available for the preparation of analogous chlorine esters having primary alkyl groups, namely, the interaction of boron trichloride with alcohols, ethers, or trialkyl borates in appropriate proportions (Wiberg and Sütterlin, *Z. anorg. Chem.*, 1931, **202**, 1, 22, 31; Gerrard and Lappert, *J.*, 1951, **2545**; 1952, **1486**) the first two could not be applied in the fluorine system, since both alcohols and ethers form co-ordination complexes of types BF_3,ROH, $BF_3,2ROH$, BF_3,R_2O (for references see Greenwood and Martin, *Quart. Reviews*, 1954, **8**, 1).

The present paper deals with the *n*-butyl series. Boron trifluoride reacted readily with tri-*n*-butyl borate, 2 mols. of the gas being absorbed and *n*-butyl difluoroboronite obtained in good yield: $(BuO)_3B + 2BF_3 \longrightarrow 3BuO{\cdot}BF_2$. When ½ mol. of the gas was used, the reaction took the same course and not according to $2(BuO)_3B + BF_3 \longrightarrow 3(BuO)_2BF$; neither was the fluoroboronate obtained by reaction of the borate and the difluoroboronite: $(BuO)_3B + BuO{\cdot}BF_2 \longrightarrow 2(BuO)_2BF$, although both these reactions proceeded quantitatively and readily (*e.g.*, at −80°) in the corresponding chlorine systems (Gerrard and Lappert, *loc. cit.*). It is possible that the elusiveness of the fluoroboronate is due to its disproportionation, and therefore the borate and difluoroboronite were mixed at −80° and pyridine was added in an effort to " fix " the equilibrium as a pyridine complex. However, the reaction observed was that given by the difluoroboronite (see below). A final attempt to isolate the fluoroboronate was by reaction of the difluoroboronite with *n*-butanol, the chlorine system $[BuO{\cdot}BCl_2 + BuOH \longrightarrow (BuO)_2BCl + HCl]$ being again taken as an analogy. The reaction actually proceeded as follows:

$$3BuOH + 3BuO{\cdot}BF_2 \longrightarrow BF_3,(BuO)_3B,BuOH + BF_3,2BuOH$$

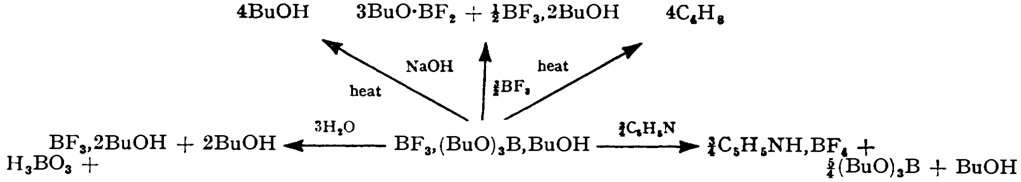
Addition of excess of *n*-butanol to the difluoroboronite gave the same products. Hydrolysis of the difluoroboronite also yielded boron trifluoride–di-*n*-butanol:

$$2BuO{\cdot}BF_2 + 3H_2O \longrightarrow BF_3,2BuOH + H_3BO_3 + HF \text{ (not isolated)}$$

whereas reaction with solid sodium hydroxide gave *n*-butanol quantitatively.

On heating the difluoroboronite at 120° for 30 hr., disproportionation (72%) was observed: $3BuO{\cdot}BF_2 \longrightarrow 2BF_3 + (BuO)_3B$. With pyridine, no co-ordination compound could be isolated, by contrast again with the dichloroboronite (Lappert, *J.*, 1953, 667), but pyridine–boron trifluoride and *n*-butyl borate were obtained: $3BuO{\cdot}BF_2 + 2C_5H_5N \longrightarrow BF_3,C_5H_5N + (BuO)_3B$.

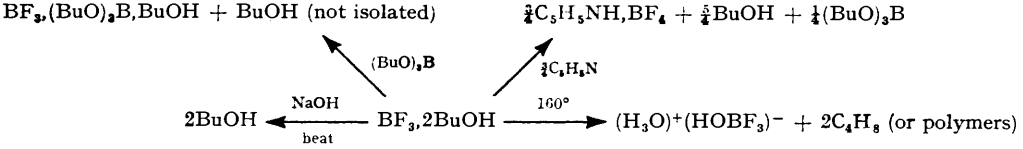
The 1 : 1 : 1 *Boron Trifluoride*–n-*Butanol–Tri*-n-*butyl Borate Complex.*—This represents a new type of 1 : 1 : 1 boron trifluoride co-ordination compound (see Greenwood and Martin, *loc. cit.*), whose composition was suggested by the following reactions:



It is a colourless liquid, which fumes slightly in moist air. On hydrolysis of this complex, boron trifluoride–di-*n*-butanol was obtained as shown above, but as this itself also underwent hydrolysis the yields were not quantitative. The 1 : 2 compound was also obtained by reaction with boron trifluoride, the difluoroboronite being the other product. Reaction with solid sodium hydroxide under reflux converted all butoxy-groups into *n*-butanol. Pyridinium tetrafluoroborate was obtained as a white precipitate by reaction with pyridine in *n*-pentane, tri-*n*-butyl borate and *n*-butanol being the other products. The 1 : 1 : 1 compound was quite unaffected by 3 hours' heating at 180°, but prolonged heating at this temperature afforded butene and a smaller quantity of higher olefins, probably polybutenes.

The composition of the 1 : 1 : 1 complex was further confirmed by the following synthesis: $BuOH + (BuO)_3B + BF_3 \longrightarrow BF_3,(BuO)_3B,BuOH$, a quantitative yield being obtained.

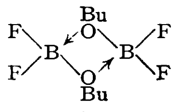
Boron Trifluoride–Di-n-*butanol.*—The formulation is in agreement with the following reaction scheme:



When the complex was heated with solid sodium hydroxide both the butoxy-groups were converted into *n*-butanol, but heating it alone at 160° for 15 min. resulted in complete decomposition to olefin (32% butene; 47% polybutenes) and hydroxonium trifluorohydroxyborate (Greenwood and Martin, *loc. cit.*). This was probably contaminated with 5—10% of difluorodihydroxyboric acid, $H^+[(OH)_2BF_2]^-$, which is obtained slowly by heating the hydroxonium fluorohydroxyborate (McGrath, Stack, and McCusker, *J. Amer. Chem. Soc.*, 1944, **66**, 1263). The polymerisation of olefins in the presence of boron trifluoride or its complexes has been reported in B.P., 1936, 453,854, and the decomposition of boron trifluoride–di-*sec.*-alcohol complexes to give the corresponding olefin and hydroxonium fluorohydroxyborate has been mentioned by Meerwein and Pannwitz (*loc. cit.*). The physical constants obtained by these workers for the hydroxonium fluorohydroxyborate and its dioxan complex were used to identify the same compound in this investigation, and in addition a pyridine derivative was prepared by addition of pyridine. This is probably a 1 : 1 : 1 compound of composition BF_3,H_2O,C_5H_5N: $C_5H_5N + BF_3,2H_2O \longrightarrow BF_3,H_2O,C_5H_5N + H_2O$.

Even on milder heating, boron trifluoride–di-*n*-butanol decomposed; *e.g.*, a specimen of b. p. 85°/7 mm. (oil-bath at 110°), n_D^{20} 1·3725, d_4^{20} 1·049, was contaminated with about 9% of the fluorohydroxyborate (b. p. 72—74°/7 mm.). When distilled at 46·5°/0·1 mm. (oil-bath at 70°), it was 98·2% pure (n_D^{20} 1·3776, d_4^{20} 1·026). The estimates of purity were confirmed by the reaction with pyridine, by which almost theoretical quantities of *n*-butanol and tri-*n*-butyl borate were obtained, but the pyridine precipitate was more than expected for pyridinium tetrafluoroborate and was in fact a mixture of the latter and the pyridine derivative of hydroxonium fluorohydroxyborate formed as shown above from fluorohydroxyboric acid.

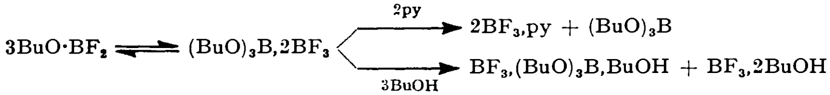
Boron trifluoride–di-*n*-butanol was synthesised by Meerwein and Pannwitz (*loc. cit.*) by passing boron trifluoride gas through *n*-butanol until the correct weight was absorbed: $2BuOH + BF_3 \longrightarrow BF_3,2BuOH$, but it is now estimated that their material was only of about 93% purity, the remainder again being essentially hydroxonium fluorohydroxyborate. This synthetic material was shown to be identical with that obtained from difluoroboronite and pyridine. On repetition of Meerwein and Pannwitz's experiment, the undistilled material (d_4^{20} 1·0053, n_D^{20} 1·3799) was shown to be very pure.



(I)

*Structures and Reaction Sequences.**—Like methyl difluoroboronite (Allen and Sugden; Goubeau and Lücke; *locc. cit.*), the *n*-butyl compound is also dimeric. Structure (I), similar to that proposed for the methyl ester, represents its probable constitution.

The reactions of *n*-butyl difluoroboronite may perhaps be better understood if a borate–boron trifluoride complex, $(BuO)_3B,2BF_3$, is postulated as an intermediate. Such compounds have been observed by Meerwein *et al.* (*loc. cit.*) and are very unstable, disproportionating to difluoroboronites: $(BuO)_3B,2BF_3 \rightleftharpoons 3BuO{\cdot}BF_2$. The reactions of the difluoroboronite with pyridine and *n*-butanol could then be represented as displacement reactions by the following schemes:



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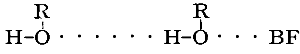
* The author is indebted to a referee for some of the suggestions contained in this section, and for suggesting the advisability of determining the conductivity of the ternary complex.

Meerwein (*Ber.*, 1933, **66**, 411) has shown that addition of boron trifluoride–di-*n*-butanol to nitrobenzene markedly increases its conductivity. This is indicative of a salt-like structure, and since the 1 : 2 complexes with boron trifluoride with methanol and with *n*-propanol have been proved to be of type (II) (Greenwood and Martin, *J.*, 1953, 757, 1427), it appears probable that the *n*-butyl compound is analogous in structure, and not of type (III) or of the type (IV), proposed by Meerwein and Pannwitz (*loc. cit.*), which accounts for the structure in terms of hydrogen-bonding. Thus boron trifluoroide–di-*n*-butanol is probably *n*-butoxonium *n*-butoxytrifluoroborate, but as no direct evidence is available, non-committal nomenclature has been used in this paper.

$(ROH_2)^+(RO\cdot BF_3)^-$
(II)

$(R_2OH)^+(HO\cdot BF_3)^-$
(III)



$$\overset{R}{\underset{|}{}}\!H\text{–}\overset{R}{O}\cdots\cdots H\text{–}\overset{R}{O}\cdots BF_3$$

(IV)

Greenwood and Martin (*Quart. Reviews*, 1954, **8**, 1) have suggested that 1 : 1 : 1 complexes of boron trifluoride are ionic; *e.g.*, the complexes $BF_3,ROR',R''F$ (Meerwein *et al.*, *J. pr. Chem.*, 1937, **147**, 251; 1939, **154**, 83) were considered to have structure $[RR'R''O]^+BF_4^-$. The observation now made (p. 790) that the complex $BF_3,(BuO)_3B,BuOH$ conducts electricity in the molten state would support a salt-like structure also for this complex. The specific conductivity of $\kappa_{20} = 9{\cdot}4 \pm 0{\cdot}4 \times 10^{-4}$ ohm^{-1} cm.$^{-1}$ is equivalent to a molar conductivity $\lambda_{M,20}$ of $3{\cdot}76 \pm 0{\cdot}16 \times 10^{-1}$ ohm^{-1} cm.^{2}. This molar conductivity is of the same order as that of boron trifluoride complexes whose structures have been proved to be ionic (*e.g.*, $BF_3,2Pr^nOH$ is $[Pr^nOH_2]^+[Pr^nO\cdot BF_3]^-$ and $\lambda_{M,25} = 6{\cdot}8 \times 10^{-1}$ ohm^{-1} cm.^{2}; Greenwood and Martin, *loc. cit.*). Possible structures would be (V) or (VI). These indicate tri-*n*-butyl borate solvation of a proton (V) or a *n*-butylcarbonium cation (VI), presumably by the attraction of these cations for the lone pairs of electrons on the oxygen atoms of the borate molecule. Although no evidence is available to distinguish between these possibilities, (V) appears the more probable. This view is taken because for all boron trifluoride complexes, whose structures have been evaluated, where there has been an apparent possibility of either a proton or a carbonium cation, the former has proved to be the true structure (*e.g.*, $BF_3,MeOH$ is $H^+[BF_3\cdot OMe]^-$ and not $Me^+[HO\cdot BF_3]^-$). Moreover, if (II) is assumed as the structure of boron trifluoride–di-*n*-butanol, then the easy interconversions of this with the 1 : 1 : 1 complex are better appreciated in terms of (V), and the reactions may then be considered as cationic displacement reactions, according to the following schemes:

$[(BuO)_3BH]^+[BuO\cdot BF_3]^-$
(V)

$[(BuO)_3B\cdot Bu^n]^+[HO\cdot BF_3]^-$
(VI)

$$[BuOH_2]^+[BuO\cdot BF_3]^- + (BuO)_3B \longrightarrow [(BuO)_3BH]^+[BuO\cdot BF_3]^- + BuOH$$

$$[(BuO)_3BH]^+[BuO\cdot BF_3]^- + 3H_2O \longrightarrow H^+[BuO\cdot BF_3]^-\ \text{(unstable)} + 3BuOH + H_3BO_3$$

$$\longrightarrow [BuOH]_2^+[BuO\cdot BF_3]^-$$

EXPERIMENTAL

Interaction of Boron Trifluoride and Tri-n-*butyl Borate.*—(*a*) Boron trifluoride (*Inorg. Synth.*, 1939, **1**, 21) was passed through tri-*n*-butyl borate (12·30 g.) at 0° until no more gas was absorbed (1 hr.). The increase in weight was 7·40 g. (Calc. for BF_3, 2 mols.: 7·64 g.). On distillation n-*butyl difluoroboronite* (17·64 g., 90%), b. p. 56—59°/35 mm., was collected, which on redistillation had b. p. 43°/11 mm., n_D^{22} 1·3858, d_4^{20} 1·122 (Found: C, 39·6; H, 7·6; F, 30·7. $C_4H_9OBF_2$ requires C, 39·4; H, 7·5; F, 31·1%).

(*b*) In another experiment the trifluoride was passed through the ester (20·00 g.) until 2·60 g. of the gas had been absorbed (Calc. for BF_3, $\frac{1}{2}$ mol.: 2·96 g.). Distillation afforded *n*-butyl difluoroboronite (6·92 g., 99%), b. p. 55—57°/32 mm., n_D^{18} 1·3893, a middle fraction (1·61 g.), b. p. 60—113°/32 mm., n_D^{19} 1·4040, tri-*n*-butyl borate (13·81 g.), b. p. 113—115°/19 mm., n_D^{19} 1·4100 (Found: B, 4·70. Calc. for $C_{12}H_{27}O_3B$: B, 4·72%), and residue (0·27 g.). The yields in these experiments are based on $(BuO)_3B + 2BF_3 \longrightarrow 3BuOBF_2$.

The molecular weight of the difluoroboronite, determined cryoscopically in *cyclo*hexane, showed the compound to be dimeric (Found: *M*, 256, 248. Calc. for $C_8H_{18}O_2B_2F_4$: *M*, 244).

Action of Pyridine on n-*Butyl Difluoroboronite.*—To the difluoroboronite (4·60 g., 3 mols.)

in *n*-pentane (5 c.c.), pyridine (1·99 g., 2 mol.) was added at –80°, and the mixture was set aside for 24 hr. at 20°. The crystals (3·51 g., 95%) obtained, which were insoluble in *n*-pentane and ligroin but soluble in chloroform, were those of pyridine–boron trifluoride, m. p. 42—44° (Found: C_5H_5N, 53·7; F, 39·4. Calc. for C_5H_5N,BF_3: C_5H_5N, 53·7; F, 38·8%); the pentane filtrate afforded tri-*n*-butyl borate (2·53 g., 86%), b. p. 110—114°/20 mm., n_D^{19} 1·4112 (Found: B, 4·77%). The yield in this experiment is calculated on $3BuO{\cdot}BF_2 + 2C_5H_5N \longrightarrow 2C_5H_5N,BF_3 + (BuO)_3B$.

Action of Sodium Hydroxide on n*-Butyl Difluoroboronite.*—The difluoroboronite (8·70 g.) and sodium hydroxide (14·3 g.; a large excess) were heated at 130° for 3 hr., and then at 130°/0·5 mm. for 2 hr.; a mixture (5·90 g.) of *n*-butanol and water condensed in a trap cooled to –80°. When dried (Na_2SO_4) this afforded *n*-butanol (5·25 g., 99%), b. p. 114—117°/760 mm., n_D^{19} 1·4012.

Thermal Stability of n*-Butyl Difluoroboronite.*—The difluoroboronite (16·90 g.) was heated at 120° for 30 hr., a potassium hydroxide absorption tube being attached to the condenser. A loss of weight (4·55 g.) was observed, and boron trifluoride (4·53 g., 72%) [Found: B, 0·721 g. Calc. for BF_3 (4·53 g.): B, 0·721 g.] was trapped in the absorption tube. Distillation of the residue (12·27 g.) afforded unchanged *n*-butyl difluoroboronite (3·70 g., 22%), b. p. 55—60°/30 mm., n_D^{20} 1·3892, a middle fraction (1·40 g.), b. p. 65—75°/14 mm., n_D^{20} 1·3943, tri-*n*-butyl borate (7·12 g., 67%), b. p. 113—116°/14 mm., n_D^{19} 1·4108 (Found: B, 4·8%), and residue (0·09 g.). The yields in this experiment are based on $3BuO{\cdot}BF_2 \longrightarrow (BuO)_3B + 2BF_3$, and of this reaction 72% has taken place (based on the weight of BF_3) under the stated conditions.

Interaction of n*-Butyl Difluoroboronite and Tri-*n*-butyl Borate: An Attempt to establish the Existence of Di-*n*-butyl Fluoroboronate.*—The borate (7·91 g., 1 mol.) was added to the difluoroboronite (4·20 g., 1 mol.) at –80°, and the mixture kept at this temperature for 1 hr.; pyridine (10·9 g., 4 mols.) in *n*-pentane (30 c.c.) was then added. Two layers were formed: the upper, pentane layer on distillation afforded tri-*n*-butyl borate (10·48 g., 99%), b. p. 114—116°/18 mm., n_D^{20} 1·4103 (Found: B, 4·7%). The lower layer slowly deposited crystals of pyridine–boron trifluoride (3·31 g., 98%), m. p. 44° (Found: C_5H_5N, 54·2%).

Action of n*-Butanol on* n*-Butyl Difluoroboronite.*—(*a*) The alcohol (27·3 g., 1 mol.) was added to *n*-butyl difluoroboronite (44·9 g., 1 mol.) at 20°. No hydrogen fluoride was evolved, but there was some heat of reaction. On distillation two main fractions were isolated: the 1 : 1 : 1 *compound* between boron trifluoride, *n*-butanol, and tri-*n*-butyl borate (44·3 g., 97%), b. p. 67—69°/12 mm., n_D^{20} 1·3980, d_4^{20} 0·929 (Found: C, 51·4, 52·6; H, 10·5, 10·3. $C_{16}H_{37}O_4B_2F_3$ requires C, 51·6; H, 10·1%); a middle fraction (2·86 g.), b. p. 74—88°/12 mm., n_D^{20} 1·3842; and *boron trifluoride–di-*n*-butanol* (21·8 g., 82%), b. p. 85—85·5°/7 mm., n_D^{20} 1·3725, d_4^{20} 1·049 (Found: C, 40·8, 41·2; H, 9·25, 9·60. $C_8H_{20}O_2,BF_3$ requires C, 44·4; H, 9·3%).

(*b*) The experiment was repeated, but distillation was carried out at 0·1 mm./<70° (bath temp.). The boron trifluoride–di-*n*-butanol, distilled three times, had b. p. 46·5—47°/0·1 mm., n_D^{20} 1·3776, d_4^{20} 1·026 (Found: C, 43·7; H, 9·60%).

(*c*) *n*-Butanol (3·81 g., 2 mols.) was added to *n*-butyl difluoroboronite (3·14 g., 1 mol.) at 20°, and hydrogen fluoride was not evolved. After 1 hr. at 20° the mixture gave on distillation *n*-butanol (1·94 g.), b. p. 39—45°/17 mm., the above 1 : 1 : 1 compound (3·26 g. Calc.: 3·20 g.), b. p. 67—70°/16 mm., n_D^{20} 1·3940, and boron trifluoride–di-*n*-butanol (1·51 g., 82%), b. p. 92—93°/16 mm., n_D^{20} 1·3760. The yields in these experiments are based on $3BuOH + 3BuO{\cdot}BF_2 \longrightarrow BF_3,(BuO)_3B,BuOH + BF_3,2BuOH$.

Hydrolysis of n*-Butyl Difluoroboronite.*—From a number of experiments, it was found that the action of a limited quantity of water on the difluoroboronite afforded boron trifluoride–di-*n*-butanol, and that the best yields were obtained in the following typical experiment: water (2·48 g., 3 mols.) was added to the difluoroboronite (11·18 g., 2 mols.) at –80° and the mixture was heated at 100—110° for 4 hr. No hydrogen fluoride was evolved. Boric acid (1·797 g.) (Found: B, 17·3. Calc. for H_3BO_3: B, 17·5%) was filtered off, diethyl ether being used to wash the precipitate. The solvent was removed from the filtrate. Distillation afforded a forerun (1·55 g.), b. p. 72—84°/13 mm., the crude 1 : 2 *n*-butanol compound (8·59 g., 82%), b. p. 84—90°/13 mm., and a residue (0·35 g.). During the early stages of the distillation, a gas (possibly hydrogen fluoride) was evolved, and boric acid deposited Redistillation of the second fraction afforded a pure specimen of boron trifluoride–di-*n*-butanol (5·60 g.), b. p. 89—90°/13 mm., n_D^{18} 1·3727, d_4^{20} 1·048. The yield in this experiment is based on $2BuO{\cdot}BF_2 + 3H_2O \longrightarrow BF_3,2BuOH + H_3BO_3 + HF$.

Titration of an aqueous solution of the difluoroboronite against standard sodium hydroxide solution could not be used as an estimation, but titration in the presence of mannitol with phenolphthalein as indicator gave constant values and the equivalent was 67·5.

Interaction of Pyridine and the 1 : 1 : 1 *Complex.*—Pyridine (1·39 g., 4 mols.) in *n*-pentane (10 c.c.) was added to the boron compound (8·70 g., 4 mols.) at −80°. A white precipitate was formed instantly, and the mixture was set aside for 1 hr. at 20°. The precipitate, pyridinium fluoroborate (2·69 g., 92%), m. p. 210—211° (Found : C_5H_5N, 47·2. Calc. for C_5H_5N,HBF_4 : C_5H_5N, 47·3%), was filtered off. The solvent was removed from the filtrate by evaporation at 20 mm., and the residue on distillation afforded *n*-butanol (0·68 g. Calc. : 0·43 g.), b. p. 26—30°/8 mm., n_D^{19} 1·4192, a middle fraction (0·28 g.), b. p. 30—98°/8 mm., n_D^{20} 1·4112, and tri-*n*-butyl borate (6·56 g., 97%), b. p. 98—99°/8 mm., n_D^{20} 1·4090 (Found : B, 4·71%). The yields in this experiment are based on $4[BF_3,(BuO)_3B,BuOH] + 3C_5H_5N \longrightarrow 3C_5H_6NBF_4 + 5(BuO)_3B + BuOH$.

Action of Sodium Hydroxide on the 1 : 1 : 1 *Complex.*—A mixture of solid sodium hydroxide (15·1 g. ; large excess) and the boron compound (7·61 g.) was heated at 130° under reflux for 3 hr., and then at 130°/0·3 mm. for a further 6 hr. A mixture (6·0 g.) of water and *n*-butanol was condensed in a trap at −80° and when dried (Na_2SO_4) this afforded *n*-butanol (5·40 g., 89%), b. p. 114—117°/760 mm., n_D^{20} 1·4006. The yield in this experiment is based on $BF_3,(BuO)_3B,BuOH \longrightarrow 4BuOH$.

Interaction of Boron Trifluoride and the 1 : 1 : 1 *Complex.*—Boron trifluoride gas was bubbled into the boron compound (10·00 g.) at 20° until saturated. The reaction was exothermic ; and distillation afforded *n*-butyl difluoroboronite (9·45 g., 96%), b. p. 40—43°/10 mm., n_D^{18} 1·3845, d_4^{20} 1·122, a middle fraction (0·32 g.), b. p. 45—82°/10 mm., n_D^{18} 1·3873, and boron trifluoride–di-*n*-butanol (2·91 g., 100%), b. p. 83—85°/10 mm., n_D^{18} 1·3720, d_4^{20} 1·050. The yield here is based on $2[BF_3,(BuO)_3B,BuOH] + 3BF_3 \longrightarrow BF_3,2BuOH + 6BuO{\cdot}BF_2$.

Hydrolysis of the 1 : 1 : 1 *Complex.*—Water (2·13 g., 3 mols.) was added to the boron compound (14·67 g., 1 mol.) at 20° ; a vigorous reaction ensued and a white precipitate of boric acid (1·475 g.) (Found : B, 17·3. Calc. for H_3BO_3 : B, 17·5%) was formed at once. The filtrate afforded unchanged 1 : 1 : 1 complex (7·1 g.), b. p. 37—38°/0·1 mm., n_D^{20} 1·3988, d_4^{20} 0·926, and boron trifluoride–di-*n*-butanol (2·84 g., 64%), b. p. 48—49°/0·1 mm., n_D^{20} 1·3734, d_4^{20} 1·040. A condensate (5·00 g.), n_D^{20} 1·3910, was collected at −80°, and on distillation a forerun (1·4 g.), b. p. 92—93°/760 mm., probably the water–*n*-butanol azeotrope, and *n*-butanol (2·90 g.), b. p. 116—117°/760 mm., n_D^{20} 1·3998, were collected. The yield is based on $BF_3,(BuO)_3B,BuOH \xrightarrow{3H_2O} BF_3,2BuOH + H_3BO_3 + 2BuOH$.

Thermal Degradation of the 1 : 1 : 1 *Complex.*—The boron compound (11·27 g.) was heated, a cold trap at −80° being connected to the outlet of the condenser. During 3 hr. with the heating-bath at 180° no condensate had collected, but after 14 hr. *n*-butene (5·14 g., 75% based on total conversion of alkyl group into olefin) (Found : *M*, 59·7. Calc. for C_4H_8 : *M*, 56·0) had collected in the trap. Its identity was confirmed qualitatively by its decolorising effect on bromine, and quantitatively by the conversion of 2·70 g. into the dibromide (9·95 g., 96%), b. p. 164—166°/760 mm., d_4^{20} 1·803, by addition of a chloroformic solution of bromine, washing with aqueous sodium hydrogen sulphite, and fractional distillation from the solvent. The only fraction isolated (1·00 g.) from the residue had b. p. 72—140°/10 mm., n_D^{20} 1·4353, decolorised bromine-water, and was probably a mixture of polymerised olefins.

Synthesis of the 1 : 1 : 1 *Complex.*—Boron trifluoride (4·61 g., 1 mol.) was passed into a mixture of tri-*n*-butyl borate (15·59 g., 1 mol.) and *n*-butanol (5·00 g., 1 mol.) at 20°. The reaction was exothermic, and the mixture was set aside for 2 hr. Distillation afforded the 1 : 1 : 1 complex (24·10 g., 96%), b. p. 73—74°/22 mm., n_D^{20} 1·3977, d_4^{20} 0·929, and a residue (0·24 g.). The yield in this experiment is calculated on $(BuO)_3B + BuOH + BF_3 \longrightarrow BF_3,(BuO)_3B,BuOH$.

Equivalent Weights of the 1 : 1 : 1 *Complex and of Boron Trifluoride–Di*-n-*butanol.*—Both of these compounds had a characteristic acidity in water. On titration with sodium hydroxide, with phenolphthalein as indicator and in the presence of mannitol, the equivalents were 121·0 for the 1 : 1 : 1 complex (Calc. : *M*, 367) and 71·0 for boron trifluoride–di-*n*-butanol (Calc. : *M*, 216).

Interaction of Pyridine and Boron Trifluoride–Di-n-*butanol.*—Pyridine (2·55 g., 3·72 mols.) in *n*-pentane (10 c.c.) was added to the boron compound (7·61 g., 4 mols.) at −80°. A white precipitate was formed instantly, and after the mixture had been stored at 20° for 1 hr., this was filtered off and washed with pentane. The precipitate (5·258 g. Calc. : 4·415 g. of $C_5H_6NBF_4$) (Found : C_5H_5N, 47·2%) was a mixture of pyridinium tetrafluoroborate and the pyridine derivative of hydroxonium fluorohydroxyborate (see p. 790). The pentane filtrate on distillation afforded *n*-butanol (3·00 g., 92%), b. p. 116—117°/760 mm., n_D^{18} 1·4023, a middle fraction (0·20 g.), b. p. 32—97°/8 mm., n_D^{18} 1·4063, and tri-*n*-butyl borate (1·62 g., 71%), b. p. 98—98·5°/8 mm., n_D^{18} 1·4110 (Found : B, 4·65%). There was a residue (0·05 g.). The yields are based on $4(BF_3,2BuOH) + 3C_5H_5N \longrightarrow 3C_5H_6NBF_4 + 5BuOH + (BuO)_3B$.

*Action of Sodium Hydroxide on Boron Trifluoride–Di-*n*-butanol.*—A mixture of the boron compound (6·32 g.) and solid sodium hydroxide (4·28 g.) was heated at 130° for 24 hr. and then at 130°/0·5 mm. for a further 4 hr. A condensate (4·10 g.) of *n*-butanol (3·70 g., 86%), b. p. 115—117°/760 mm., and water was collected in a trap at −80°. The yield in this experiment is based on $BF_3,2BuOH \longrightarrow 2BuOH$.

*Lack of Reaction between Boron Trifluoride and Boron Trifluoride–Di-*n*-butanol.*—Boron trifluoride was bubbled through the boron compound (11·70 g.) for 2 hr. The mixture was evacuated (8 mm.) and distilled, the unchanged boron compound (11·54 g., 99%), b. p. 80—82°/8 mm., n_D^{19} 1·3720, d_4^{20} 1·064, being obtained.

*Interaction of Tri-*n*-butyl Borate and Boron Trifluoride–Di-*n*-butanol.*—The borate (5·97 g., 1 mol.) and boron trifluoride–di-*n*-butanol (5·60 g., 1 mol.) were mixed at 20° and no heat change was observed. The mixture was set aside for 1 hr. at 20° and was then distilled, yielding the 1 : 1 : 1 compound (9·35 g., 98%), b. p. 67°/12 mm., n_D^{20} 1·3972, a middle fraction (0·30 g.), b. p. 67—85°/12 mm., and boron trifluoride–di-*n*-butanol (1·00 g.), b. p. 89°/12 mm., n_D^{20} 1·3764. The yield of 1 : 1 : 1 complex is based on $(BuO)_3B + BF_3,2BuOH \longrightarrow BF_3,(BuO)_3B,BuOH + BuOH$.

*Thermal Degradation of Boron Trifluoride–Di-*n*-butanol.*—The boron compound (7·70 g.) was heated (bath at 160°) for 15 min. *n*-Butene (1·27 g., 32%) was collected at −80° and characterised as the dibromide, b. p. 163—165°/760 mm., d_4^{20} 1·800. The remainder separated into two layers. The upper layer (2·60 g.) yielded a mixture of what are believed to be polybutenes (1·87 g., 47%), b. p. 30—150°/0·5 mm., n_D^{20} 1·4565, d_4^{20} 0·824 (Found : I.V., 263), and a waxy olefinic residue (0·43 g., 11%), which declorised bromine. The lower layer (3·73 g.), a dark red oil, afforded hydroxonium fluorohydroxyborate (3·00 g., 81%), b. p. 72—74°/7 mm., n_D^{25} 1·3235, d_4^{20} 1·624, as a viscous liquid, and a dark residue remained. The last-named compound was further characterised as the dioxan derivative, m. p. 138—140° (after 3 crystallisations from ether). Meerwein and Pannwitz (*loc. cit.*) give m. p. 142°. Yields in this experiment are based on $BF_3,2BuOH \longrightarrow BF_3,2H_2O + 2C_4H_8$ (and polymers).

Pyridine Derivative of Hydroxonium Fluorohydroxyborate.—Pyridine (1·315 g., 1·19 mol.) in *n*-pentane (10 c.c.) was added dropwise to hydroxonium fluorohydroxyborate (1·3940 g., 1 mol.) at −80°. The sticky, white precipitate was washed with ether. It (2·1029 g., 95%) was believed to be *pyridinium trifluorohydroxyborate* (Found : C_5H_5N, 46·4. $C_5H_7ONBF_3$ requires C_5H_5N, 47·8%).

*Synthesis of Boron Trifluoride–Di-*n*-butanol.*—Boron trifluoride (6·61 g., 1 mol.) was passed into *n*-butanol (15·05 g., 2 mols.) at 20°. The undistilled boron trifluoride–di-*n*-butanol had n_D^{20} 1·3799, d_4^{20} 1·0053 (Found : C, 44·3; H, 9·3%). On distillation, the fraction of b. p. 86°/8 mm. (19·52 g.) was collected; n_D^{20} 1·3722, d_4^{20} 1·041.

*Repetition of the Pyridine Experiment on Synthetic Boron Trifluoride–Di-*n*-butanol.*—(*a*) Pyridine (3·20 g., 1·34 mol.) in *n*-pentane (20 c.c.) was added dropwise to the undistilled boron compound (8·661 g., 1 mol.), prepared as above, at −80°. The mixture was set aside for 1 hr. at 20°, and pyridinium tetrafluoroborate (5·0259 g., 100%), m. p. 212° (Found : C_5H_5N, 47·2%), was filtered off and thoroughly washed with more pentane. (*b*) The experiment was repeated upon the distilled synthetic material (4·6337 g.) and pyridine (2·00 g.). The precipitate (3·0470 g. Calc. : 2·684 g.) had m. p. 200—208° (Found : C_5H_5N, 46·5%).

Electrical Conductivity of the 1 : 1 : 1 *Complex.*—The cell was dried in the oven for 1 hr. at 110° and filled with the highly purified sample (after a preliminary rinse) in a dry cabinet under a nitrogen atmosphere. The electrodes (platinum) were left in the cell for ½ hr. after the first reading to make certain there was no change due to progressive hydrolysis. The conductivity of the molten $(BuO)_3B,BuOH,BF_3$ was $9·4 \pm 0·4 \times 10^{-4}$ ohm⁻¹ cm.⁻¹ at 20°.

The author thanks Messrs. E. H. Reynolds and J. K. Anderson, of the Research Organisation of British Insulated Callender's Cables Ltd., for very kindly carrying out the conductivity measurement, and Dr. W. Gerrard for encouragement and helpful discussion.

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[*Received, July* 10*th*, 1954.]