637. *The Interaction of Boron Trichloride with Unsaturated Alcohols and Ethers.*

By W. GERRARD, M. F. LAPPERT, and H. B. SILVER.

Interaction of unsaturated alcohols (allyl, methallyl) (1, 2, and 3 mols., severally) with boron trichloride (1 mol.) gave the appropriate dichloroboronites, chloroboronates, and trialkenyl orthoborates. The alkenyloxyboron chlorides, which were also obtained from the borates and boron trichloride, were unstable, decomposing to the appropriate chloroalkene, but stable 1 : 1 and 1 : 2 complexes were obtained with pyridine. Neither these borates nor tripropynyl borate was attacked by hydrogen chloride at 20°, but at 120° triallyl borate was dealkylated. Dealkylation by both hydrogen bromide and hydrogen iodide was accompanied by addition. Diallyl and dimethallyl ethers were easily cleaved by boron trichloride; the mixed allyl methallyl ether reacted by methallyl-oxygen fission. Neither ammonia nor pyridine co-ordinated with triallyl borate, and the reaction with bromine was slow. General resemblance to saturated systems has been noted.

STUDIES [1] on boron trichloride–alcohol and –ether systems have been extended to unsaturated compounds. The reactions of allyl and methallyl alcohols and their mixed and simple ethers and of propynol show a broad similarity to those of corresponding saturated systems, except that certain reactions are accompanied by addition. The allyl and the methallyl group appear to have reactivities intermediate between those of *sec.*- and *tert.*-alkyl groups.

Triallyl borate,[2] obtained in poor yield, is the only borate previously prepared by the interaction of boron trichloride and an unsaturated alcohol, although the preparation of triallyl [3] and trimethallyl [4] borate from other starting materials has been described.

Allyl, methallyl, and propynyl orthoborate have now been prepared in good yield by addition of boron trichloride (1 mol.) to the appropriate alcohol (3 mols.) in *n*-pentane at −80°; the reverse order of addition was less successful. By alteration of the relative proportions of the reagents evidence of the formation of intermediate alkenyloxyboron chlorides was obtained:

$$\mathrm{BCl_3} \longrightarrow \mathrm{RO{\cdot}BCl_2} \longrightarrow \mathrm{(RO)_2BCl} \longrightarrow \mathrm{B(OR)_3}$$

Of the alkenyloxyboron chlorides, the dichloroboronites, $\mathrm{RO{\cdot}BCl_2}$, could not be adequately characterised owing to their instability, but stable 1 : 2 complexes with pyridine, and in the allyl system also a 1 : 1 complex, were obtained. The chloroboronates, $\mathrm{(RO)_2BCl}$, whilst still unstable, were not as easily decomposed as the dichloroboronites; a 1 : 2 complex with pyridine was obtained from diallyl chloroboronate, whilst the dimethallyl compound afforded a 1 : 1 complex. The alkenyloxyboron chlorides were also obtained from the appropriate orthoborate and boron trichloride; their decomposition followed the general scheme observed earlier in saturated systems: [1b, 5, 6]

$$\mathrm{B(OR)_3} \xrightarrow{\mathrm{BCl_3}} \mathrm{(RO)_2B{\cdot}Cl} \xrightarrow{\mathrm{BCl_3}} \mathrm{RO{\cdot}BCl_2}$$

$$\mathrm{3RO{\cdot}BCl_2} \longrightarrow \mathrm{3RCl + B_2O_3 + BCl_3}$$

$$\mathrm{3(RO)_2BCl} \longrightarrow \mathrm{3RCl + B_2O_3 + B(OR)_3}$$

Pyrolysis of the 1 : 1 complex between allyl dichloroboronite and pyridine was similar to that observed with the *n*-butyl analogue,[7] whilst the 1 : 1 complex between dimethallyl

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[1] Gerrard and Lappert, *J.*, 1951, (*a*) 1020; (*b*) 2545; (*c*) 1952, 1486; Edwards, Gerrard, and Lappert, *J.*, 1955, 1470.

[2] Councler, *J. prakt. Chem.*, 1871, **18**, 371.

[3] Rothstein and Saville, *J.*, 1952, 2987.

[4] Thomas, *J.*, 1946, 882.

[5] Gerrard and Lappert, *J.*, 1955, 3084.

[6] Lappert, *J.*, 1956, 1768.

[7] *Idem*, *J.*, 1953, 667.

chloroboronate and pyridine disproportionated to give the 1 : 2 dichloroboronite complex. Such a complex was also obtained from triallyl borate, boron trichloride, and pyridine, the chloro-ester being added to pyridine in excess to enhance the formation of the 1 : 2 complex.

Like most other orthoborates, the unsaturated ones are hydrolysed readily to give orthoboric acid and the appropriate alcohol. Neither with ammonia nor with pyridine was there evidence for co-ordination with triallyl borate (cf. Colclough, Gerrard, and Lappert [8] for orthoborate co-ordination reactions):

$$\mathrm{RO{\cdot}BCl_2,py \longrightarrow RCl + BOCl,py}$$

$$\mathrm{2(RO)_2BCl,py \longrightarrow RO{\cdot}BCl_2,2py + B(OR)_3}$$

$$\mathrm{B(OR)_3 + 2BCl_3 \longrightarrow 3RO{\cdot}BCl_2 \xrightarrow{6py} 3(RO{\cdot}BCl_2,2py)}$$

Whereas trialkyl borates, except those possessing a very reactive α-carbon atom, such as tri-*tert.*-butyl borate (which is dealkylated instantly at room temp.), do not react with hydrogen chloride,[1b] triallyl, trimethallyl, and tripropynyl borate did not react with hydrogen chloride at 20°, but triallyl borate after 14 hours at 120° afforded allyl chloride, 1 : 2-dichloropropane, presumably formed by addition of hydrogen chloride to the former, and boric acid. Hydrogen bromide reacted with triallyl borate at 20° by dealkylation and addition, as was made evident by isolation of allyl bromide and tri-3-bromopropyl borate. The corresponding iodo-products were obtained when hydrogen iodide was employed, but the tri-3-iodopropyl borate could not be adequately purified. The anti-Markownikoff addition is probably explained by an electromeric effect in the allylic double bond of the borate in the direction of the boron atom, encouraged by the electron-attracting power of that atom.

$$\mathrm{(CH_2{:}CH{\cdot}CH_2{\cdot}O)_3B + 3HHal} \begin{array}{l} \nearrow \mathrm{3CH_2{:}CH{\cdot}CH_2Hal + B(OH)_3} \\ \searrow \mathrm{(Hal{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}O)_3B} \end{array}$$

Although allyl alcohol instantly reacted with 0·3N-bromine in carbon tetrachloride, no addition was observed with the orthoborate under these conditions. This is not the case [9] with many other allyl esters (*e.g.*, acetate and phthalate). In substantially more concentrated solutions a near quantitative yield of tri-2 : 3-dibromopropyl borate was obtained (see also ref. 10).

Both diallyl and dimethallyl ether readily reacted with boron trichloride at low temperature by fission. At –80°, a white solid was formed in each case, probably the ether–trichloride complex, but this was too unstable to be characterised.

$$\mathrm{ROR + BCl_3 \longrightarrow [1:1\ Complex] \longleftrightarrow RCl + RO{\cdot}BCl_2 \longrightarrow RCl + [BOCl]}$$

$$\mathrm{3ROR + 2BCl_3 \longrightarrow 6RCl + B_2O_3}$$

The reaction of boron trichloride with the mixed allyl methallyl ether was investigated, because it had previously been shown [1c] that the more electron-releasing of the alkyl groups in a mixed dialkyl ether gave the chloroalkane, whilst the dichloroboronite resulted from the other group. As the alkenyl dichloroboronites are not stable (see above), the trichloride and ether were mixed in the proportions 1 : 2, in order that the orthoborate, which was the known product of chloroboronate decomposition, could be identified. The isolation of triallyl borate indicates that methallyl–oxygen fission had occurred. This suggests that the methallyl group is the more electron-releasing, probably owing to the additional $+I$ effect of the methyl group.

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[8] Colclough, Gerrard, and Lappert, *J.*, 1955, 907.
[9] Boyd and Roach, *Analyt. Chem.*, 1947, **19**, 158.
[10] Councler, *Ber.*, 1877, **10**, 1655.

EXPERIMENTAL

Preparations and Techniques.—Dimethallyl ether and allyl methallyl ether were prepared by Tamele, Ott, Marple, and Hearne's method.[11] Hydrogen chloride was generated from dry ammonium chloride and concentrated sulphuric acid, hydrogen bromide by Gerrard's method,[12] and hydrogen iodide from phosphorus, iodine, and water. The hydrogen halides were dried by passage through phosphoric oxide. Boron trichloride was distilled before use. Chlorine attached to boron, and boron, were estimated by hydrolysis and acidimetric titration, and halogen in alkenyl halides by the Volhard method after hydrolysis by ethanolic sodium hydroxide in sealed tubes. Pyridine in complexes (which were all washed with pentane, then dried at reduced pressure) was estimated by steam-distillation from sodium hydroxide solution and titration of the distillate with sulphuric acid (bromophenol-blue).

Preparation of Orthoborates.—Trimethallyl borate (93%), b. p. 118°/19 mm., m. p. 29·5—30° (Found : B, 4·84. Calc. for $C_{12}H_{21}O_3B$: B, 4·83%), was obtained by dropwise addition of boron trichloride (1 mol.) in *n*-pentane (6 mols.) to the alcohol (3 mols.) at −80°, followed by immediate removal of volatile matter at 15°/15 mm. When pyridine (3 mols.) was mixed with the alcohol the yield of borate was 58%, owing to formation of the pyridine–boron trichloride compound. *Triprop-2-yn-1-yl borate* (94%), b. p. 99°/12 mm., n_D^{20} 1·4540, d_4^{10} 1·040 (Found : C, 61·3; H, 5·2; B, 6·17. $C_9H_9O_3B$ requires C, 61·4; H, 5·1; B, 6·15%), was likewise obtained in absence of pyridine. Triallyl borate (85%), b. p. 76°/15 mm., n_D^{21} 1·4276, d_4^{20} 0·926 (Found : B, 5·9. Calc. for $C_9H_{15}O_3B$: B, 5·9%), was likewise obtained, except that methylene dichloride (about 2 mols.) was the solvent. The yield of borate was 58% when the order of mixing was reversed. When allyl alcohol (1 mol.) was added dropwise to boron trichloride (1 mol.) at −80°, the mixture being allowed to remain at 20° for 2 hr., allyl chloride (85%), b. p. 45° (Found : Cl, 46·2. Calc. for C_3H_5Cl : Cl, 46·4%), was removable at 15°/15 mm. and there was a residue containing boron equivalent to boron trioxide (1·81 g., 100%).

Interaction of the Orthoborates and Boron Trichloride.—The reactants were mixed at −80° in the proportions appropriate to the formation of the dichloroboronite or the chloroboronate. Specimens in sealed tubes were stored at 20° and at stated times (Table) the loss of easily hydrolysable chlorine was determined and interpreted as extent (%) of decomposition of the chloro-ester according to the reactions : $B(OR)_3 + 2BCl_3 \longrightarrow 3RO{\cdot}BCl_2 \longrightarrow 3RCl + [3BOCl \longrightarrow B_2O_3 + BCl_3]$; $2B(OR)_3 + BCl_3 \longrightarrow 3(RO)_2BCl \longrightarrow 3RCl + [3RO{\cdot}BO \longrightarrow B(OR)_3 + B_2O_3]$.

System * no.	$B(OR)_3$ (mol.)	BCl_3 (mol.)	R	Decomposition (%), time in hr.							
				0·25	0·5	1	3	20	27	44	50
1	1	2	C_3H_5	94·3	—	97·1	—	—	—	—	—
2	1	2	C_4H_7	90·9	91·8	—	—	—	—	—	—
3	2	1	C_3H_5	—	20	—	—	37	43	47·5	51
4	2	1	C_4H_7	—	5	—	11	—	31	35·5	36

* Each system equivalent to 3 mols. of chloro-ester.

Freshly mixed reactants no. 3, after being heated for 4 hr. at 100° under reflux, afforded allyl chloride (77%) (Found : Cl, 46·0%), triallyl borate (77·7%), b. p. 82—84°/20 mm. (Found : B, 6·01%), and boron trioxide. Similarly system no. 2 (120° for 15 min.) gave methallyl chloride (78%), b. p. 71—72°, n_D^{20} 1·4284 (Found : Cl, 38·5. Calc. for C_4H_7Cl : Cl, 39·2%), boron trichloride (82%), and boron trioxide (91%). System no. 1, prepared in *n*-pentane (6 mols.) at −80°, immediately afforded, on addition of pyridine (3 mols.), the 1 : 1 *pyridine–allyl dichloroboronite complex* (94%), m. p. 61° (Found : Cl, 30·2; B, 5·1; C_5H_5N, 37·5. $C_8H_{10}ONCl_2B$ requires Cl, 32·5; B, 4·95; C_5H_5N, 36·3%), as a white solid (sparingly soluble in water), which (3·08 g.) at 150° (5·5 hr.) gave allyl chloride (0·53 g.) and a solid (2·45 g.), insoluble in *n*-pentane, comprising the water-reactive pyridine–boron oxychloride complex (Found : Cl, 24·6; B, 6·1; C_5H_5N, 54·7. Calc. for C_5H_5ONClB : Cl, 25·1; B, 7·65; C_5H_5N, 56·0%), and an insoluble substance (Found : Cl, 25·2; B, 9·0; C_5H_5N, 52·3%). System no. 1 in *n*-pentane, added to pyridine (6 mols. in *n*-pentane 10 mols.), gave the *dipyridine–allyl dichloroboronite complex* (95% after being at 15°/0·4 mm.) (Found : Cl, 22·4; B, 3·8; C_5H_5N, 50·8. $C_{13}H_{15}ON_2Cl_2B$ requires Cl, 23·9; B, 3·6; C_5H_5N, 53·2%) as an easily hydrolysable white solid.

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[11] Tamele, Ott, Marple, and Hearne, *Ind. Eng. Chem.*, 1941, **33**, 115.
[12] Gerrard, *Research*, 1954, **7**, S 20.

To system no. 3, prepared in methylene dichloride (6 mols.) at −80°, pyridine (3 mols. in the same solvent, 3 mols.) was added at −80°. Volatile matter was removed at 15°/15 mm., and the residue comprised the pyridine–allyl dichloroboronite 1 : 1 complex (100%) (Found : Cl, 29·8; B, 4·81; C_5H_5N, 36·2%), insoluble in *n*-pentane; triallyl borate (91%) and pyridine (69%) were extracted by *n*-pentane. When system no. 3 in *n*-pentane was added to pyridine (6 mols.) in *n*-pentane, the *dipyridine–diallyl chloroboronate compound* (80%) (Found : Cl, 11·9; C_5H_5N, 50·6. $C_{16}H_{20}O_2N_2ClB$ requires Cl, 12·0; C_5H_5N, 49·7%) was obtained as a white solid. The system no. 2 prepared at −39°, added to pyridine (6 mols.) at −80°, afforded the *dipyridine–methallyl dichloroboronite compound* (80%, after being at 15°/15 mm.) (Found : Cl, 22·4; C_5H_5N, 49·5. $C_{14}H_{17}ON_2Cl_2B$ requires Cl, 22·8; C_5H_5N, 50·8%), a readily hydrolysable white solid. To system no. 4, prepared in methylene dichloride, pyridine (3 mols.) was added at −80°. Volatile matter was removed at 15°/10 mm., leaving the solid *pyridine–dimethallyl chloroboronate compound* (95%) (Found : Cl, 12·1; B, 3·97; C_5H_5N, 29·4. $C_{13}H_{19}O_2NClB$ requires Cl, 13·3; B, 4·04; C_5H_5N, 29·6%), which after being heated at 120° (4 hr., reflux), afforded at 15°/0·4 mm. a liquid (0·49 g.), a mixture of trimethallyl borate (4·43 g., 93%), m. p. 27·5° (Found : B, 4·88%) (extracted by *n*-pentane), and a residue of crude dipyridine–dichloroboronite complex (6·1 g.) (Found : Cl, 25·0; B, 4·1; C_5H_5N, 45·1%).

Certain Properties of Triallyl Borate.—The borate (1·99 g.) was recovered after hydrogen chloride had been passed through it for 3·5 hr. at 15°, but at 120° (14 hr.) allyl chloride (1·08 g.), dichloropropane (0·73 g.), b. p. 93·5°, n_D^{19} 1·4310, triallyl borate (0·20 g.), b. p. 59°/13 mm., and boric acid (0·48 g.) were obtained. After hydrogen bromide had been passed (8 hr.) into the borate (4·78 g.) at 20°, matter volatile at 15°/15 mm. was condensed (3·87 g.) and separated into allyl bromide (3·61 g.), b. p. 66° (Found : Br, 65·8. Calc. for C_3H_5Br : Br, 66·1%), and dibromopropane (0·18 g.), b. p. 60°/16 mm. The less volatile residue (6·96 g.) was separated by methylene dichloride into boric acid (0·73 g.) and *tri-3-bromopropyl borate* (6·15 g.), b. p. 112°/0·01 mm. (Found : Br, 55·4; B, 2·53. $C_9H_{18}O_3Br_3B$ requires Br, 56·5; B, 2·55%), which on hydrolysis afforded 3-bromopropan-1-ol, b. p. 78°/17 mm., n_D^{17} 1·4863 (Found : Br, 57·0. Calc. for C_3H_7OBr : Br, 57·5%). Hydrogen iodide was passed into the borate (3·57 g.) (0·67 hr.) at 20°, whereupon allyl iodide (2·5 g.), n_D^{18} 1·5094 (Found : I, 73·8. Calc. for C_3H_5I : I, 75·6%), was obtained as a condensate at 15 mm., and the residue (4·48 g.) comprised boric acid (0·18 g.) (separated by methylene dichloride), triallyl borate (1·32 g.), b. p. 80°/18 mm. (Found : B, 5·78%), and a final residue of tri(iodopropyl) borate (2·1 g.) (Found : I, 65·8. Calc. for $C_9H_{18}O_3I_3B$: I, 67·4%). On hydrolysis and extraction with ether, the iodo-alcohol could not be isolated owing to constant liberation of iodine.

Triallyl borate (2·56 g., 1 mol.) did not react with bromine (0·3N) in carbon tetrachloride, but did so at 5° with bromine (6·75 g., 3 mols.) in the same solvent (25 c.c.). After removal of volatile matter at 15°/10 mm., tri-2 : 3-dibromopropyl borate (8·83 g., 95%), m. p. −16° (Found : Br, 71·3; B, 1·64. Calc. for $C_9H_{15}O_3Br_6B$: Br, 72·5; B, 1·64%), was obtained as an undistillable, viscous, orange liquid, readily hydrolysed to 2 : 3-dibromopropanol, b. p. 109°/19 mm., n_D^{20} 1·5557, d_4^{16} 2·138.

Interaction of Ethers and Boron Trichloride.—(a) *Diallyl ether.* The ether (5·02 g., 3 mols.) was added (25 min.) to boron trichloride (4·00 g., 2 mols.) at −80°. A white solid was formed, but disappeared on warming. Allyl chloride (6·6 g., 84%), b. p. 46° (Found : Cl, 46·2%), was obtained as a condensate (15 mm.), after prior heating to ensure complete decomposition of chloroboronate, and there was a residue (1·90 g.) containing boron trioxide (1·10 g., 93%).

Addition of diallyl ether (5·17 g., 1 mol.) in *n*-pentane (20 c.c.) to boron trichloride (6·18 g., 1 mol.) in *n*-pentane (20 c.c.) at −80° gave a white precipitate. At −20° this began to decompose exothermally, and therefore was immediately cooled. Addition of pyridine (4·17 g., 1 mol.) at −80° gave pyridine–boron trichloride (2·40 g.), m. p. 109°, insoluble in *n*-pentane and in cold water.

(b) *Dimethallyl ether.* The ether (7·60 g., 3 mols.) was slowly (25 min.) added to the trichloride (4·71 g., 2 mols.) at −80°. Similar observations were made as in (a) and a similar method yielded methallyl chloride (8·06 g., 74%), b. p. 72°, n_D^{20} 1·4279 (Found : Cl, 38·9%), and boron trioxide (1·32 g., 95%).

(c) *Allyl methallyl ether.* The ether (5·28 g., 2 mols.) was added (15 min.) to the trichloride (2·76 g., 1 mol.) in *n*-pentane (15 c.c.) at −80°. Volatile matter was removed (15°/10 mm.) and a brown viscous liquid remained. This was distilled to give triallyl borate (1·36 g., 96%), b. p. 58°—65°/9 mm. (Found : B, 5·8%), and a residue of boron trioxide (0·73 g., 100%).

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