312. *Further Investigations in the Butenyl–Boron Trichloride System.*

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The present together with earlier work [1, 2] constitutes a systematic investigation of the reactions of boron trichloride with allylic alcohols, ethers, and borates, and of the properties of allylic borates, chloroboronates, and dichloroboronites. The systems now reported are the 1- and the 3-methylallyl. For comparison with a non-allylic system, certain analogous reactions involving but-3-enyl compounds were also carried out. The results are discussed and it is concluded that the 1- and the 3-methylallyl group have electron-releasing power (3- > 1-) intermediate between those of typical *sec.*- and *tert.*-alkyl groups; by contrast the but-3-enyl is scarcely more electron-releasing than the *n*-butyl group. Allylic rearrangements producing methylallyl chlorides were observed and are considered to be of S_N1' type; an alcoholysis with tri-3-methylallyl borate indicated C–O fission.

The present paper supplements our earlier studies [1, 2] of the interaction of boron trichloride and allylic alcohols, ethers, and borates and of the properties of allylic borates $B(OR)_3$, chloroboronates $BCl(OR)_2$, and dichloroboronites $BCl_2{\cdot}OR$. Previously, the allyl, 2-methylallyl, and prop-2-ynyl systems were reported : [1, 2] the present investigation is concerned with the 1- and 3-methylallyl and the but-3-enyl system. These reactions are now available for comparison with corresponding ones involving saturated compounds.[3-8] Our purpose has been to demonstrate the influence of the allylic double bond on the reactivity of the 1-carbon atom, to show how this is modified when a methyl group is present in the 1-, 2-, or 3-position, to indicate how this effect is further modified when the double bond is in a more remote position (but-3-enyl system), and to obtain information regarding the mechanisms of those reactions wherein C–O fission was possible, by noting any anionotropic changes in the 1- and 3-methylallyl systems.

Tri-1- and -3-methylallyl borate were prepared from boric acid, benzene, and the appropriate alcohol [for a discussion of this method see ref. (9)]. Attempted preparation of the same borates from boron trichloride [see (1)] using the conventional technique [see ref. (9)] was unsuccessful, reaction (2) being observed instead.* Tri-1-methylallyl borate was however obtained in 58% yield, when the formed hydrogen chloride was removed instantly at low temperature and no solvent was present. The conventional method provided a nearly quantitative yield of tribut-3-en-1-yl borate.

$$BCl_3 + 3ROH \longrightarrow B(OR)_3 + 3HCl \tag{1}$$

$$BCl_3 + 3ROH \longrightarrow 3RCl + B(OH)_3 \tag{2}$$

Tri-1- and -3-methylallyl borates were readily hydrolysed [see (3)], and reacted with octan-1-ol [see (4)], whereas with hydrogen chloride there was no reaction at room temperature; at 110°, however, tri-3-methylallyl borate was dealkenylated [see (5)].

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* The composition (*i.e.*, relative percentages of 1- and 3-methylallyl compounds) of the product is shown in Table 2 and similarly for subsequent reactions involving 1- and 3-methylallyl derivatives.

[1] Gerrard, Lappert, and Silver, *J.*, 1956, 3285.
[2] *Idem, J.*, 1956, 4987.
[3] Gerrard and Lappert, *J.*, 1951, 1020.
[4] *Idem, ibid.*, p. 2545.
[5] Lappert, *J.*, 1956, 1768.
[6] Gerrard and Lappert, *J.*, 1955, 3084.
[7] Lappert, *J.*, 1953, 667.
[8] Gerrard and Lappert, *J.*, 1952, 1486; Edwards, Gerrard, and Lappert, *J.*, 1955, 1470; 1957, 377; Abel, Edwards, Gerrard, and Lappert, *J.*, 1957, 501.

Interaction between boron trichloride and the borates in the proportions indicated by schemes (6) and (7) afforded alkenyloxyboron chlorides only in the but-3-enyl system; these were reasonably stable at room temperature. With the methylallyl borates the isolated products indicated instant decomposition according to schemes (8) and (9). Attempts to show that alkenyloxyboron chlorides had been formed, by preparing (stable) pyridine complexes at −80°, was successful only for di-1-methylallyl chloroboronate.

$$B(OR)_3 + 3H_2O \longrightarrow 3ROH + B(OH)_3 \tag{3}$$

$$B(OR)_3 + 3C_8H_{17}{\cdot}OH \longrightarrow B(O{\cdot}C_8H_{17})_3 + 3ROH \tag{4}$$

$$B(OR)_3 + 3HCl \longrightarrow 3RCl + B(OH)_3 \tag{5}$$

$$2B(OR)_3 + BCl_3 \longrightarrow 3BCl(OR)_2 \tag{6}$$

$$B(OR)_3 + 2BCl_3 \longrightarrow 3BCl_2{\cdot}OR \tag{7}$$

$$3BCl(OR)_2 \longrightarrow 3RCl + B_2O_3 + B(OR)_3 \tag{8}$$

$$3BCl_2{\cdot}OR \longrightarrow 3RCl + B_2O_3 + BCl_3 \tag{9}$$

Di-3-methylallyl ether was cleaved at low temperature by boron trichloride [see (10)].

$$3R_2O + 2BCl_3 \longrightarrow 6RCl + B_2O_3 \tag{10}$$

3-Methylallyl chloride was not affected by a trace of boron trichloride in one hour at room temperature, but a larger quantity catalytically effected addition-polymerisation. Double-bond estimation of this material, if considered as a means of end-group analysis, indicates a molecular weight of about 1450 for the product.

Discussion.—By experiments with boron compounds and allyl derivatives, we had shown [2] qualitatively that the electron-releasing power of the allyl group is intermediate between that of a primary and a secondary alkyl group. The present experiments with methylallyl compounds show that methyl substitution in the 1- or 3-position markedly increases electron-release (in contrast to substitution in the 2-position [1]), and that generally the relative electron-release of the 1- and the 3-methylallyl group is intermediate between those of a typical *sec.*-alkyl (*e.g.*, *sec.*-butyl) and a typical *tert.*-alkyl (*e.g.*, *tert.*-butyl) group. Moreover, the 3-methylallyl group (a primary one) appears to be more powerfully electron-releasing than its 1-isomer (a secondary one). Our conclusions may be compared with those, based on kinetic data obtained by studying certain reactions of allylic chlorides, of Oae and Werf,[10] Andrews and Young,[11] and Vernon.[12] Our conclusion with respect to the 1- and the 3-methylallyl group supports the earlier work,[10, 11] and not the later.[12] The results in the but-3-enyl system indicate that an olefinic double bond in the 3-position has little effect on the reactivity of the 1-carbon atom, although it appears that the but-3-enyl group is more powerfully electron-releasing than *n*-butyl. Our interpretation of reactivites is based on comparison of the reactions here described with analogous ones in saturated systems; the relevant data are summarised in Table 1. Further evidence in the methylallyl systems is based on our conclusion that in most of the reactions (see Table 2) where C–O fission was possible a carbonium cation was in fact an intermediate (S_N1' reaction), whereas most of the corresponding reactions with typical *sec.*-alkyl compounds involved S_N2 replacement on the 1-carbon atom, as demonstrated mainly by studies of Walden inversion.[3]

From Table 2 it is evident that the relative composition of the methylallyl chlorides, obtained from the reactions described, is constant (R^3Cl, 66·5 ± 2·5%; R^1Cl, 33·5 ± 2·5%; R^3 and R^1 = 3- and 1-methylallyl respectively) irrespective of the nature (*i.e.*, 1- or 3-methylallyl) of the starting compounds. This can only reasonably be accounted for by

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[9] Lappert, *Chem. Rev.*, 1956, **56**, 959.

[10] Oae and VanderWerf, *J. Amer. Chem. Soc.*, 1953, **75**, 2724.

[11] Andrews and Young, *ibid.*, 1944, **66**, 421.

[12] Vernon, *J.*, 1954, 423.

TABLE 1.

Reaction	Results		Ref.
	Typical primary or *sec.*-alkyl	Typical *tert.*-alkyl	
BCl_3 + 3ROH ...	Scheme (1)	Scheme (2)	3, 4
Schemes (3) & (4)	Reaction involves B–O fission	Reaction mechanism may involve C–O fission (not yet demonstrated)	3, 13
Scheme (5)	No reaction	Rapid reaction at 20°	3, 4
Scheme (8)	Chloroboronates are stable at 20° (primary more stable than secondary at high temperature)	No evidence for existence of chloroboronate	5
Scheme (9)	Primary dichloroboronites stable at 20°, unlike secondary which, however, at −80° form stable complexes with pyridine	No evidence for existence of dichloroboronite	6, 7

TABLE 2.*

Allylic rearrangements were observed in the 1- and 3-methylallyl systems in the reactions listed.

Reaction no.	3	5	5	6	9	9	11
R in reactant	R^3	R^3	R^1	R^3	R^1	R^3	R^3
Composition of product (%)	R^3Cl 68 R^1Cl 32	R^3OH 91·3 ± 0·5 R^1OH 8·7 ± 0·5	R^1OH 100	R^3Cl 69 R^1Cl 31	R^3Cl 69 R^1Cl 31	R^3Cl 66 R^1Cl 34	R^3Cl 64 R^1Cl 36

* R^1 and R^3 = 1- and 3-methylallyl.

assuming that each reaction involves an intermediate carbonium cation (11), which being mesomeric, is identical irrespective of the nature of the source, that is to say each reaction is of S_N1' type.[14] These conclusions support our earlier views that the analogous reactions

$$(11) \qquad CH_3{-}CH{=}CH{-}CH_2^{+} \longleftrightarrow CH_3{-}\overset{+}{C}H{-}CH{=}CH_2$$

in saturated systems, when involving strongly electron-releasing alkyl groups, proceeded by S_N1 mechanisms. The formation of the carbonium cation in the decomposition of the alkenyloxyboron chlorides, and in the dealkenylation of tri-3-methylallyl borate substantiate the mechanisms previously suggested.[3-6] The present results are similar to those of Catchpole and Hughes;[15] by ethanolysis of 1- and 3-methylallyl chlorides, under conditions favouring pre-ionisation, identical mixtures of ethers were obtained. The isolation of a mixture of methylallyl chlorides, having the above composition, in a future investigation may be used as evidence of an S_N1' reaction.

Experiments on esterification, hydrolysis, and alcoholysis, with one exception (see Table 2), did not lead to rearranged products. This suggests that these reactions involved B–O and not C–O fission. The exception was alcoholysis (octan-1-ol) of tri-3-methylallyl borate; the result suggests that some C–O fission was involved. This is the first example of such a reaction in the boron system.

The effect of boron trichloride on 3-methylallyl chloride is probably understandable in terms of a standard cationic polymerisation mechanism. Thus the 3-methylallyl chloride may, in the first instance, be functioning as co-catalyst, producing with boron trichloride a carbonium cation, which is then available for initiation of polymerisation [cf. ref. (16)].

EXPERIMENTAL

Preparations and Techniques.—3-Methylallyl alcohol was prepared by Nystrom and Brown's procedure[17] (reduction of crotonaldehyde with lithium aluminium hydride); a by-product,

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[13] Scattergood, Miller, and Gammon, *J. Amer. Chem. Soc.*, 1945, **67**, 2150.

[14] Ingold, "Structure and Mechanism in Organic Chemistry," G. Bell and Sons, London, 1953, p. 586.

[15] Catchpole and Hughes, *Trans. Faraday Soc.*, 1941, **37**, 629.

[16] Pepper, *Quart. Rev.*, 1954, **8**, 88.

[17] Nystrom and Brown, *J. Amer. Chem. Soc.*, 1947, **69**, 1197.

not previously reported, was di-3-methylallyl ether, the identity of which was established analytically and by infrared spectroscopy. But-3-en-1-ol was obtained in low yield by passing formaldehyde vapour into allylmagnesium bromide and conventional working-up. Procedures for purification of starting materials and analytical methods have been described previously.[1,2,3] Mixtures of 1- and 3-methylallyl chloride were analysed by the refractive-index method,[18] and of 1- and 3-methylallyl alcohols by infrared spectroscopy. As the composition of mixtures has been given in Table 2, such mixtures will be referred to non-committally in the experimental part as butenyl chlorides or alcohols.

Preparation of Borates.—A mixture of the alcohol (3 moles), boric acid (1 mole), and benzene (30 c.c.) was carefully fractionated, a modified Dean and Stark head being used for removal of the first fraction, comprising the benzene–water azeotrope, and subsequently a total-reflux partial take-off head for separation of the succeeding fractions (benzene and *borate*). The results are shown in Table 3.

TABLE 3.

R in $B(OR)_3$	Yield (pure) (%)	B. p./mm.	$n_D^{(t)}$	$d_D^{(t)}$	Found (%)			Required (%)		
					C	H	B	C	H	B
1-Methylallyl ...	73	78°/10	(20)1·4177	(18)0·8717	64·7	9·2	4·8	64·4	9·4	4·8
3-Methylallyl ...	81	112°/9	(25)1·4428	(15·5)0·9160	64·5	9·2	4·8	64·4	9·4	4·8

Interaction of Alcohols and Boron Trichloride [*Reactions* (1) *and* (2)].—(a) *But*-3-*en*-1-*ol*. The trichloride (4·30 g., 1 mol.) in *n*-pentane (10 c.c.) at $-35°$ was added during 10 min. to the alcohol (8·11 g., 3 mols.) in *n*-pentane (25 c.c.) at $-80°$. Volatile matter was removed at 20°/15 mm. and subsequent distillation afforded *tribut*-3-*en*-1-*yl borate* (7·89 g., 94%), b. p. 112°/15 mm., n_D^{20} 1·4332, d_4^{22} 0·8925 (Found : C, 64·4; H, 9·4; B, 4·8%).

(b) 1-*Methylallyl alcohol.* The trichloride (3·09 g., 1 mol.) in *n*-pentane (10 c.c.) at $-35°$ was added during 15 min. to 1-methylallyl alcohol (5·70 g., 3 mols.) in *n*-pentane (20 c.c.) at $-80°$. The resulting mixture, a white solid and a colourless liquid, was warmed to 20° and kept at this temperature for 15 hr. Volatile matter was removed at 20°/15 mm. and subsequent distillation of the remainder (3·40 g.) afforded impure tri-1-methylallyl borate (0·32 g., 4·6%), b. p. 40—43°/14 mm. (Found : B, 3·01%), and a residue of boric acid (1·53 g., 94%).

The experiment was repeated with identical procedure, except that volatile matter wa s removed directly after completion of addition; this gave 15·1% of borate. When no solvent was used, however, and again volatile matter was rapidly removed, the borate was obtained in 58% yield.

(c) 3-*Methylallyl alcohol.* The alcohol (8·76 g., 3 mols.) was added during 40 min. to the trichloride (4·75 g., 1 mol.) at $-80°$; the reaction was violent and boron trichloride (0·68 g.) which escaped was collected. Butenyl chloride (6·70 g., 70%), n_D^{25} 1·4263 (Found : Cl, 39·3. Calc. for C_4H_7Cl : Cl, 39·3%), was collected as a condensate at $-80°$ and a residue of boric acid (2·11 g., 98%) was obtained after the mixture had been at 18°/5 mm.

Chemical Properties [*Reactions* (3)—(5)] *of Borates.*—(a) *Hydrolysis.* When water (0·54 g., 1 mol.) was added to tri-1- and tri-3-methylallyl borate (2·24 g., 3 mols.) severally and the mixture evacuated at 20°/0·01 mm., the corresponding alcohol (96·3% and 99%, respectively) was obtained as a condensate at $-80°$, leaving boric acid (100%) as a residue.

(b) *Alcoholysis.* Octan-1-ol (7·80 g., 3 mols.) was added to each borate (4·48 g.) severally. Tri-1-methylallyl borate afforded 1-methylallyl alcohol (4·19 g., 97%) as a condensate, tri-*n*-octyl borate (5·75 g., 72·3%), b. p. 222°/28 mm., and a residue (1·01 g.), whereas tri-3-methylallyl borate, after similar working-up, gave butenyl alcohol (3·74 g., 87%), n_D^{20} 1·4250, and tri-*n*-octyl borate (7·33 g., 92%), b. p. 178°/0·25 mm. (Found : B, 2·71. Calc. for $C_{24}H_{51}O_3B$: B, 2·72%).

(c) *Dealkenylation.* Tri-1-methylallyl borate was recovered quantitatively, after hydrogen chloride had been passed into it continuously at 18° (1 hr.) and subsequently at 120° (4 hr.).

Tri-3-methylallyl borate did not react with hydrogen chloride at 15° during 10 hr. When the gas was passed through this borate (7·21 g.) at 110° (4 hr.), boric acid (1·97 g., 99%) remained in the reaction vessel and butenyl chloride (6·10 g., 70%), n_D^{20} 1·4290 (Found : Cl, 39·2%), was collected in a trap at $-80°$.

Interaction between Trialkenyl Borates and Boron Trichloride [*Reactions* (6) *and* (7)].—(a) *But*-3-*en*-1-*yl*. The trichloride (0·90 g., 1 mol.) was added to the borate (3·44 g., 2 mols.)

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[18] Eisner and Young, *ibid.*, 1941, **63**, 2113.

at −80°, whereupon *dibut-3-en-1-yl chloroboronate* was formed in quantitative yield; it had b. p. 47°/0·2 mm., n_D^{20} 1·4338, d_4^{23} 0·9745 (Found: Cl, 18·4; B, 5·78. $C_8H_{14}O_2ClB$ requires Cl, 18·8; B, 5·74%).

By similar procedure, *but-3-enyl dichloroboronite* was obtained quantitatively from boron trichloride (2·70 g., 2 mols.) and the borate (2·58 g., 1 mol.); it had b. p. 36°/15 mm., n_D^{20} 1·4261 (Found: Cl, 44·5; B, 7·01. $C_4H_7OCl_2B$ requires Cl, 46·4; B, 7·08%).

(b) 1- *and* 3-*Methylallyl.* Attempted preparation of the chloroboronates and dichloroboronites by means of reactions (6) and (7) was unsuccessful owing to the low stability [see reactions (8) and (9)] of these compounds. Thus when each borate (2 mols.) was mixed at −80° with boron trichloride (1 mol.), a sample withdrawn from each mixture revealed that 94—95% decomposition according to scheme (8) had taken place within 1 min. at 20°; this was determined by analysis.

When tri-1-methylallyl borate (2·43 g., 1 mol.) was added to boron trichloride (2·55 g., 2 mols.) at −80° a vigorous reaction occurred. The mixtures was warmed to 20°. After 8 hr. at 20°/20 mm., boron trichloride (0·96 g.) was collected in a potassium hydroxide absorption tube, and a solid brown residue (3·75 g.) (Found: Cl, 6·57; B, 2·48%) remained; this was insoluble in water. We interpret this result as decomposition of 1-methylallyl dichloroboronite first formed, according to (9), followed by polymerisation of 1-methylallyl chloride by boron trichloride, a reaction independently demonstrated for the 3-isomer (see below).

Pyridine Complexes of Methylallyloxyboron Chlorides.—Pyridine (3·44 g., 3 mols.) in *n*-pentane (5 c.c.) was added to a mixture of tri-1-methylallyl borate (6·49 g., 2 mols.) and boron trichloride (1·70 g., 1 mol.) in *n*-pentane (5 c.c.) at −80°. The mixture was warmed to 20° and volatile material was removed at 20°/15 mm. The residue was washed with more *n*-pentane. Removal of solvent afforded the impure solid 1 : 1-*complex* between pyridine and di-1-methylallyl chloroboronate (8·95 g., 77%) (Found: Cl, 9·7; C_5H_5N, 29·6. $C_{13}H_{19}O_2NClB$ requires Cl, 13·2; C_5H_5N, 29·7%).

Attempted preparation, by a similar technique, of pyridine complexes of 1-methylallyl dichloroboronite and of the 3-methylallyloxyboron chlorides proved unsuccessful.

Decomposition (8) *of Bismethylallyl Chloroboronates.*—(a) *The* 1-*isomer.* Boron trichloride (3·10 g., 1 mol.) at −80° was added to tri-1-methylallyl borate (11·85 g., 2 mols.) at −80°. The mixture was warmed to 20° and, whilst in series with a cold-trap at −80°, was heated for 1 hr. at 135°, then cooled to 20° and evacuated at 20°/20 mm. Butenyl chloride (4·42 g., 62%), $n_D^{23·5}$ 1·4276 (Found: Cl, 39·0%), was collected in the trap. The remainder afforded on distillation tri-1-methylallyl borate (5·00 g., 85%), b. p. 74°/10 mm. (Found: B, 4·86%), and a residue of boric oxide (1·72 g., 93%).

(b) *The* 3-*isomer.* Tri-3-methylallyl borate (8·56 g., >2 mols.) was added to boron trichloride (1·39 g., 1 mol.) at −80°, the reaction being vigorous. After 20 hr. at 20°/15 mm., a condensate of butenyl chloride (2·38 g., 74%), n_D^{20} 1·4281 (Found: Cl, 39·0%), had collected in a trap at −80°. The remainder afforded tri-3-methylallyl borate (5·90 g., 100%), b. p. 126°/15 mm., n_D^{20} 1·4431, and a residue of boric oxide.

Stability of the But-3-enyloxyboron Chlorides.—In order to ascertain the stability at 20° of the but-3-enyloxyboron chlorides with respect to reactions (8) and (9), samples (*ca.* 0·20 g.) of the compounds, prepared as above, were withdrawn and sealed off. These were analysed after stated times for easily hydrolysable chlorine and boron; the change in the ratio of the two estimations enables the percentage decompositions to be calculated. Di-3-butenyl chloroboronate was substantially unchanged (<1% decomp.) after 22 hr. But-3-enyl dichloroboronate was 11% decomposed after 3 hr., and 92% decomposed after 21 hr.

Interaction between Bis-3-methylallyl Ether and Boron Trichloride [*Reaction* (10)].—The ether (8·07 g., 3 mols.) was added, with stirring, to the trichloride (5·00 g., 2 mols.) at −80°. A red-orange lower layer formed. The mixture was kept at 20°/10 mm. for 3½ hr. Butenyl chloride (7·60 g., 66%), n_D^{22} 1·4271 (Found: Cl, 39·3%), was collected at −80° and a residue containing boric oxide (1·47 g., 97%) remained in the reaction vessel.

Effect of Boron Trichloride on 3-Methylallyl Chloride.—The trichloride (0·05 g.) was added to 3-methylallyl chloride (6·67 g.), n_D^{20} 1·4346, at −80°. The mixture was allowed to remain at 20° for 1 hr., whereafter it was washed with water and dried ($MgSO_4$). Unchanged 3-methylallyl chloride, n_D^{20} 1·4346, was obtained.

When boron trichloride (1·10 g.) at −80° was added to 3-methylallyl chloride (5·92 g.) at −80° and the mixture allowed to warm to room temperature in series with a trap at −80°, a yellow liquid was obtained, which rapidly darkened and after 1 hr. had become a brown gum. Removal of volatile matter at 10 mm. afforded boron trichloride and a residue (5·92 g.). This was soluble in acetone, benzene, carbon tetrachloride, and ethanol, but insoluble in water. An iodine value (Wijs's method) suggested that the material has a molecular weight of 1448.

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