The Formation of Rearrangement Products in the Reactions of Cyclic Alcohols with Boron Trichloride

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The reactions of cyclopentylmethanol and cyclohexylmethanol with boron trichloride afford the corresponding dichloroborinates (alkoxydichloroboranes), which decompose thermally to yield mixtures of halide isomers: ring expansion and a 1,2-hydride shift occur. Secondary cyclic alcohols having no ring substituent other than the hydroxy-group, and 1-substituted cycloalkanols, react rapidly at room temperature or below to yield the corresponding halides with no detectable rearrangement. *trans*-2-Methylcyclohexanol affords the corresponding halide with retention of configuration, together with 15—20% of the tertiary chloride. Subsequent rearrangement of certain products is catalysed by heating with boron trichloride. The 1-methylcycloalkyl chlorides thus afford mixtures with the isomeric secondary methylcycloalkyl chlorides, whilst cycloheptyl chloride undergoes irreversible rearrangement to ring-contracted products. Primary halides are isomerized only slowly by boron trichloride.

THE reactions of alcohols with boron trichloride yield rearranged alkyl halides by decomposition of the corresponding alkyl dichloroborinates (alkoxydichloroboranes) and dialkyl chloroboronates (dialkoxychloroboranes) (Scheme 1).[1-3] From primary alcohols, the intermediate

$$\mathrm{ROH} \xrightarrow{\mathrm{BCl_3}} \mathrm{ROBCl_2} \longrightarrow \mathrm{R^+} + [\mathrm{OBCl}] + \mathrm{Cl^-} \longrightarrow \mathrm{RCl}$$

$$\mathrm{ROBCl_2} \xrightarrow{\mathrm{ROH}} \mathrm{(RO)_2BCl} \longrightarrow \mathrm{R^+} + [\mathrm{OBOR}] + \mathrm{Cl^-} \longrightarrow \mathrm{RCl}$$

SCHEME 1

chloro-esters are isolable but secondary and tertiary alcohols give alkyl chloride rapidly at or below room temperature. Cyclic alcohols have now been shown to follow similar reaction sequences although the chloro-esters are considerably more prone to disproportionation (Scheme 2) than their acyclic counterparts and yielded mixtures of esters, together with cycloalkyl chlorides,

$$6\ \mathrm{ROBCl_2} \rightleftharpoons 3\ \mathrm{(RO)_2BCl} + 3\ \mathrm{BCl_3} \rightleftharpoons 2\ \mathrm{(RO)_3B} + 4\ \mathrm{BCl_3}$$

SCHEME 2

on attempted distillation. Cyclopentylmethyl and cyclohexylmethyl dichloroborinates were therefore characterized at room temperature. Their decomposition was studied by heating them under reflux (Table 1), boron trichloride being maintained in the system in certain experiments by the use of an acetone–Cardice-cooled condenser, in order to suppress disproportionation. This also had the effect, previously observed with n-butyl and n-pentyl dichloroborinates,[2] of reducing the rate of decomposition to alkyl chloride, although the reason for this effect is not clear; Lewis acids in general catalyse the decomposition.[1,2]

TABLE 1

Thermal decomposition of cyclopentylmethyl and cyclohexylmethyl dichloroborinates

ROBCl$_2$				Volatile product analysis (mole %) [a]					
R	Wt. (g)	Temp (°C)	Time (h)	ROH [b]	(1)	(2)	(3)	(4)	(9)
$C_5H_9CH_2$	15·0	100 [c]	1 [d]	0		>99			<1
$C_5H_9CH_2$	8·5	50 [e]	0·25 [f]	84·9		11·5			3·6
			0·5	29·8		56·0	0·9	0·8	12·5
			1	0		95·8	1·2	1·1	1·8
					(5)	(6)	(7)	(8)	(10)
$C_6H_{11}CH_2$	15·3	100 [c]	6 [f]	98·5	0·1	0·4	0·9	0·01	0·1
			12	95·8	0·3	0·9	2·6	0·1	0·3
			18	81·6	1·1	2·6	12·7	0·7	1·3
			24	48·6	3·8	9·7	32·6	3·7	1·5
			30	25·7	5·8	15·4	40·0	6·8	6·3
			36	0	7·0	29·4	46·7	8·1	8·7
$C_6H_{11}CH_2$	26·3	100 [e]	3 [f]	69·8	1·4	6·5	16·7	2·3	3·2
			6	7·6	5·1	22·8	50·1	13·0 [g]	1·4
			9 [h]	0	5·7	24·4	49·5	17·7	2·7

[a] See Scheme 3; (9) = cyclohexene; (10) = methylcyclohexane (only traces of olefins detectable). [b] From hydrolysis of unchanged ROBCl$_2$. [c] Under reflux with acetone–Cardice-cooled condenser. [d] No change after a further 30 h at 100 °C. Cyclohexyl chloride (6·8 g, 0·69 mol. equiv.) (Found: Cl, 29·1. Calc. for $C_6H_{11}Cl$: Cl, 29·95%) was then isolated. [e] BCl$_3$ allowed to escape as formed. Traps (−80°) collected negligible quantities of organic products. [f] Successive periods for the given reaction. [g] The initial product was mainly the *cis*-2-isomer (64%), which isomerized to the more stable *trans*-2-isomer, and the 3- and 4-isomers, on further heating. [h] In a similar experiment, cyclohexylmethyl dichloroborinate (47·6 g) was heated for 10 h at 100 °C. Isolation of volatile products then yielded a mixture (23·9 g), n_D^{20} 1·4618 (Found: Cl, 26·2. Calc. for $C_7H_{13}Cl$: Cl, 26·8%), containing (compound, mole %): (5), 7·0; (6), 33·3; (7), 41·6; (8), 17·3; (10), 0·7. Total yields (mol. equiv.): RCl, 0·73; hydrocarbon, 0·005.

The formation of rearrangement products resulting

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[1] W. Gerrard and M. F. Lappert, *J. Chem. Soc.*, 1951, 1020, 2545; 1955, 3084.

[2] W. Gerrard, H. R. Hudson, and W. S. Murphy, *J. Chem. Soc.*, 1962, 1099; 1964, 2314.

[3] H. R. Hudson, R. R. F. Kinghorn, and W. S. Murphy, *J. Chem. Soc.* (*C*), 1971, 3593.

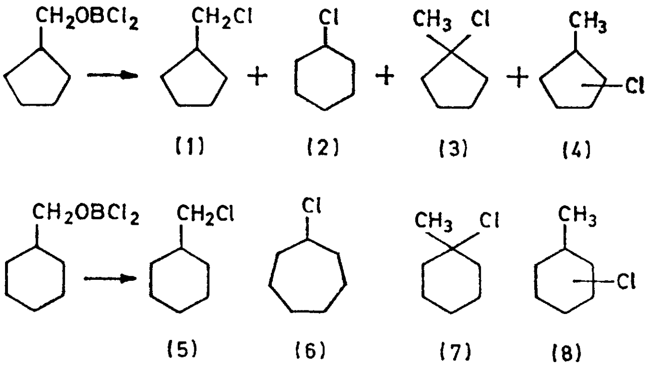
from both ring-expansion and 1,2-hydride shift (Scheme 3) is consistent with a carbonium ion mechanism and it is probable that the first-formed products were similar to those reported in studies on the thermal decomposition of the corresponding chloroformates.[4] Preponderant retention of configuration in the reaction of *trans*-2-methylcyclohexanol with boron trichloride (Table 2) indicates than an ion pair intermediate is involved (Scheme 4). The presence of boron trichloride complicates the systems by causing further reaction or rearrangement of certain products. The low olefin yield is unusual in a carbonium ion reaction although it appeared from a study of product composition as the reactions proceeded that recombination with hydrogen chloride was occurring, this probably being catalysed by the boron trichloride present. The initial composition of the substitution products derived from cyclohexylmethyl dichloroborinate is most nearly represented by that recorded after 3 h at 100 °C (Table 1), during which time boron trichloride was removed by distillation as formed. (Isomerization of products by the dichloroborinate is considerably slower.) The unrearranged (cyclohexylmethyl) and ring-expanded (cycloheptyl) chlorides were stable under these conditions, although cycloheptyl chloride underwent slow irreversible rearrangement to cyclohexylmethyl chloride and 1-, 2-, 3-, and 4-methylcyclohexyl chlorides during prolonged

TABLE 2

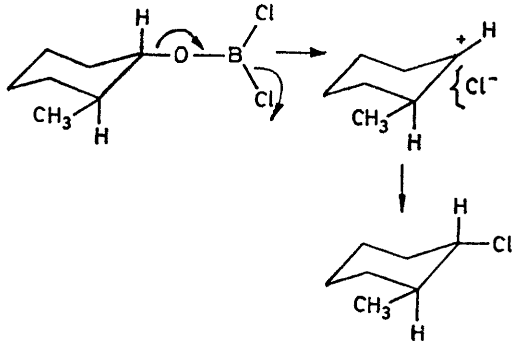
Reactions of secondary and tertiary alcohols with boron trichloride

ROH		Yields (mol. equiv.)	
R	Wt. (g)	RCl	Olefin
Cyclopentyl	30·0	0·78 [a]	0
Cyclohexyl	15·3	0·77 [a]	Trace [b]
Cycloheptyl	12·2	0·70 [a,c]	Trace [d]
1-Methylcyclopentyl	8·2	0·65 [a]	0·02 [e]
1-Methylcyclohexyl	49·0	0·74 [a]	0·09 [f]
trans-2-Methylcyclohexyl	3·2	0·32 [g,h]	0·01 [h,i]

[a] Unrearranged isomer only. [b] Cyclohexene. [c] ROH (0·05 mol. equiv.) remained. Reaction completed in 0·5 h at 100°. In a similar experiment the product had the following isomeric composition (%) after further heating (h, cycloheptyl chloride, cyclohexylmethyl chloride, secondary methylcyclohexyl chlorides, 1-methylcyclohexyl chloride): 0·5, 99·8, 0·3, 0·6, 0·3; 1·0, 98·5, 0·4, 0·6, 0·5; 1·5, 97·7, 0·9, 0·8, 0·6; 2·0, 96·6, 1·2, 1·4, 0·8. [d] Cycloheptene. [e] 1-Methylcyclopentene. [f] 1-Methylcyclohexene. [g] *trans*-2-Methylcyclohexyl chloride (84%) and 1-methylcyclohexyl chloride (16%); other isomers not detectable. [h] Yields determined by g.l.c. analysis. ROH (0·67 mol. equiv.) recovered. Reaction completed by heating (1 h) at 100 °C, to give RCl (96%) and olefin (4%), of similar composition. [i] 1-Methylcyclohexene (38%), and 3-methylcyclohexene (62%).



SCHEME 3



SCHEME 4

TABLE 3

Isomerization of cycloalkyl halides by boron halides

Halide [a]	Boron halide	(mol. equiv.)	Temp. (°C)	Time (h)	Product analysis (mole %) [a]				
					(1)	(2)	(3)	(4)	
(1)	BCl_3	0·38	50 [b]	0·5	96	4 [c]			
(3)	BCl_3	0·36	50 [b]	0·5			62	38 [c]	
					(5)	(6)	(7)	(8)	(10) [d]
(5)	BCl_3	0·51	100 [b]	50	97·5		0·9	0·5	0·3
(5)	BCl_3	0·50	100 [b]	110	95·3		2·0	2·3	
(6)	BCl_3	0·14	100 [e]	51	27·9	27·3	20·1	23·0	1·7
(6)	BCl_3	0·18	100 [b]	50	21·0	21·2	20·0	37·7	0·1
(6)	BCl_3	0·18	100 [b,f]	110	14·9		25·9	41·7	17·6
(7)	BCl_3	0·17	100 [b]	50			35·2	58·4	6·4
(7)	BCl_3	0·18	100 [b]	120			34·5	54·2	11·1
(7)	BCl_3	0·12	100 [e]	9			69·9	23·4	6·7
(7)	$C_5H_{11}OBCl_2$	10·8	100 [e]	9			85·6	14·4	

[a] See footnote *a* in Table 1. [b] In sealed ampoule. [c] Hydrocarbons not detectable. [d] $<0{\cdot}5\%$ Olefin in any product. [e] Under reflux. [f] Good first-order plots for the disappearance of cycloheptyl chloride were obtained in similar experiments by sampling and analysing at intervals of 3 h (mol. equiv. BCl_3, *k*): 0·15, $1{\cdot}01 \times 10^{-5}$ s^{-1}; 0·19, $1{\cdot}40 \times 10^{-5}$ s^{-1}; 0·29, $2{\cdot}50 \times 10^{-5}$ s^{-1}.

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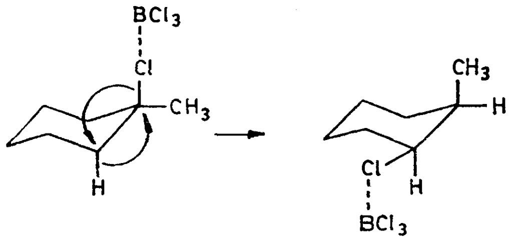
[4] W. E. Dupuy and H. R. Hudson, *J.C.S. Perkin II*, 1972, 1715.

heating with boron trichloride under reflux. The 1-methylcycloalkyl chlorides were the most susceptible to isomerization by boron trichloride and afforded equilibrium mixtures with the secondary methylcycloalkyl chlorides in under 50 h at 100 °C. Gradual isomerization of the tertiary chlorides also occurred during experiments in which boron trichloride was removed as formed.

In the cyclohexylmethyl system, the first-formed secondary halide was predominantly the *cis*-2-isomer, although this rearranged to the more stable *trans*-2-, in addition to the 3- and 4-isomers on prolonged heating. Isomerization of the tertiary halide by a concerted mechanism [5] (or alternatively *via* a short-lived ion pair), could account for this initial formation of the thermodynamically less stable halide (Scheme 5).

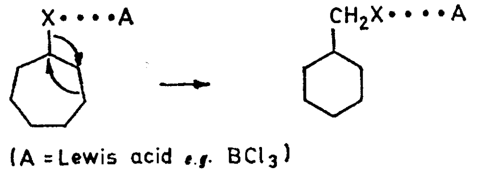


SCHEME 5

Evidence for [1,3] shifts leading directly from cycloalkylmethyl to 2-methylcycloalkyl groups (as observed in chloroformate decompositions and nitrous acid deaminations [4,6]) was therefore not obtainable in the dichloroborinate decompositions. Nor were bicyclo[*n*.1.0]-alkanes [4,6] detectable in the reaction products although this does not preclude their transitory formation, since they were shown to be unstable in the presence of boron trichloride. The major hydrocarbon by-product which was obtained in the thermal decomposition of cyclohexylmethyl dichloroborinate, and which was also formed during the isomerization of 1-methylcyclohexyl chloride and of cycloheptyl chloride by boron trichloride, was methylcyclohexane. It probably results from intermolecular hydride transfer; [7] the reactions of other cyclohexyl derivatives with aluminium trichloride similarly afford some methylcyclohexane.[8]

Secondary alcohols having no ring substituents other than the hydroxy-group (cyclopentanol, cyclohexanol, cycloheptanol), and the tertiary alcohols (1-methylcyclopentanol and 1-methylcyclohexanol) yielded only the corresponding chlorides by reaction with boron trichloride at room temperature or below. Small amounts of olefin which were formed initially underwent addition of hydrogen chloride to yield the same chlorides. 2-Methylcyclohexanol gave a mixture of chlorides containing *ca.* 15% of the tertiary isomer, further isomerization to the latter occurring at 100 °C.

Unlike the thermal decomposition of the analogous cycloheptyl chloroformate and the nitrous acid deamination of cycloheptylamine,[4,6] the cycloheptyl dichloroborinate decomposition was not accompanied by detectable ring contraction, although cycloheptyl chloride rearranged slowly to give ring-contracted products, as described above, on continued heating in the presence of boron trichloride. Cycloheptyl bromide undergoes similar rearrangement in the presence of Lucas' reagent.[9] In such cases we consider it unlikely that a primary carbonium intermediate [9] is formed. Ring contraction could involve either a protonated cyclopropane intermediate [4,6] or a concerted migration (Scheme 6).[5]



SCHEME 6

EXPERIMENTAL

Starting Materials.—Cyclopentylmethanol, cyclohexylmethanol, 1-methylcyclopentanol, and 1-methylcyclohexanol were prepared by the Grignard reaction. Cyclopentanol, cyclohexanol, cycloheptanol, and 2-methylcyclohexanol (*trans*, 75%; *cis*, 25%) were obtained commercially. The purity and identity of each were confirmed by g.l.c. on polyethylene glycol 400 and by i.r. and ^{1}H n.m.r. spectral analysis. *trans*-2-Methylcyclohexanol, b.p. 62 °C at 9 mmHg, n_D^{20} 1·4617, was separated from the *cis-trans*-mixture by fractional crystallization of the 3,5-dinitrobenzoates.[10] Boron trichloride was obtained from a cylinder (American Potash and Chemical Corp.) and redistilled.

Analytical Methods.—Volatile products (cycloalkyl chlorides and hydrocarbons) were analysed by g.l.c. on a 4 m × 1/8 in o.d. stainless steel column containing polyethylene glycol 400 (10% on 60—80 mesh HMDS Chromosorb) at 60°. Products were eluted in the same order as on silicone oil [11] and were completely resolved except for the 2-, 3-, and 4-methylcycloalkyl chlorides, some of whose peaks overlapped. Aqueous treatment of reaction products converted unchanged dichloroborinates to the corresponding alcohols, which gave separate peaks, and provided a measure of the extent of reaction.

Preparation and Decomposition of Cycloalkylmethyl Dichloroborinates.—Cyclopentylmethanol (17·0 g) was added dropwise (6 h) to boron trichloride (20·5 g, 1·2 mol. equiv.) at −70°. Volatile matter was removed under reduced pressure to leave a liquid residue of *cyclopentylmethyl dichloroborinate* (28·3 g, 0·88 mol. equiv.) (Found: Cl, 41·0. $C_6H_{11}BCl_2O$ requires Cl, 39·3%), τ 8·1—8·9 (ring protons, m) and 5·95 (*exo*-CH_2, d, J_{CH-CH_2} 6 Hz), ν 1340 (B–O) and 930 (B–Cl) cm^{-1}. Similarly, cyclohexylmethanol (15·0 g)

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[5] H. C. Brown and W. J. Wallace, *J. Amer. Chem. Soc.*, 1953, **75**, 6279.

[6] W. E. Dupuy, H. R. Hudson, and P. A. Karam, *Tetrahedron Letters*, 1971, 3193.

[7] C. D. Nenitzescu, 'Carbonium Ions,' eds. G. A. Olah and P. von R. Schleyer, Wiley, New York, 1970, ch. 13, p. 463.

[8] F. Aizawa, M. Arai, and M. Yamaguchi, *J. Chem. Soc. Japan*, 1969, **90**, 497.

[9] Yu G. Bundel, A. M. Yuldashev, and O. A. Reutov, *Izvest. Akad. Nauk S.S.S.R., Ser. Khim.*, 1969, 1397.

[10] L. M. Jackman, A. K. Macbeth, and J. A. Mills, *J. Chem. Soc.*, 1949, 1717.

[11] W. E. Dupuy, H. R. Hudson, and P. A. Karam, *J. Chromatography*, 1972, **71**, 347.

and boron trichloride (17·7 g, 1·2 mol. equiv.) gave *cyclohexylmethyl dichloroborinate* (23·4 g, 0·92 mol. equiv.) (Found: Cl, 37·1. $C_7H_{13}BCl_2O$ requires Cl, 36·5%), τ 8·1—8·9 (ring protons, m) and 6·05 (*exo*-CH_2, d, J_{CH-CH_2} 6 Hz), ν 1340 (B–O) and 920 (B–Cl) cm^{-1}. Decomposition and disproportionation occurred on attempted distillation of either product. Quantities of each were heated under reflux as specified (Table 1), samples (*ca.* 0·5 cm^3) being withdrawn periodically for analysis. Products (total or sample as appropriate) were treated cautiously with excess of water at room temperature. Organic materials were recovered by evaporation (20° C at 0·1 mmHg) and collection in cold traps (−80°) (total products), or by ether extraction (samples); they were dried (K_2CO_3) and analysed by g.l.c. as above.

Reactions of Secondary and Tertiary Cyclic Alcohols with Boron Trichloride.—The alcohol (in ether if solid) was added dropwise (4—5 h) to boron trichloride (1·1 mol. equiv.) at −70 °C. Organic products were then isolated as above and identified by chlorine analysis, refractive index, g.l.c., and i.r. spectroscopy. Results are given in Table 2.

Isomerization of Products by Boron Halides.—The cycloalkyl chlorides (1—4 g) were sealed in ampoules with boron trichloride as indicated (Table 3) and heated for the specified periods. 1-Methylcyclohexyl chloride and cycloheptyl chloride were also heated under reflux with either boron trichloride or n-pentyl dichloroborinate (Table 3). Products were analysed as above.

Bicyclo[4.1.0]heptane (1·1 g) underwent 80% decomposition when heated with boron trichloride (0·34 mol. equiv.) in an ampoule (50 °C, 0·5 h).

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