434. *Factors in the Formation of Isomerically and Optically Pure Alkyl Halides. Part III.*[1] *Alkyl Rearrangements in Alcohol–Boron Trihalide Reaction Systems.*

By W. GERRARD, H. R. HUDSON, and W. S. MURPHY.

Formation of alkyl halides by the decomposition of alkyl dihalogenoborinates and dialkyl halogenoboronates is accompanied by rearrangement of primary to secondary alkyl groups, whilst the latter are interconvertible. s-Alkyl compounds do not usually give n-alkyl halides, except that n-propyl bromide (*ca.* 8%) is formed in certain isopropyl reaction systems. Isobutyl esters afford t-butyl and, by skeletal rearrangement, s-butyl halides.

MANY covalent halides react with alcohols to yield, as final products, alkyl halides, and varying degrees of alkyl rearrangement can occur. The application of gas–liquid chromatography has revealed that there can be considerable rearrangement of primary alkyl groups (*e.g.*, of n- to s-butyl).[1] Boron halides give relatively large proportions of rearranged alkyl halides. Apart from the zinc chloride-catalysed reaction of alcohols with hydrogen chloride,[1,2] and the Friedel–Crafts alkylation of benzene,[3] the only other

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[1] Part II, Gerrard and Hudson, preceding Paper.
[2] Gerrard, Hudson, and Murphy, *J.*, 1962, 1099.
[3] Baddeley, *Quart. Rev.*, 1954, **8**, 355.

reaction shown to afford rearrangement from an n- and to an s-alkyl group is that of primary amines with nitrous acid.[4]

In reactions of boron trichloride with alcohols, the intermediate chloro-esters decompose, slowly in the case of n-alkyl compounds, and quickly with s- or t-alkyl groups, to yield alkyl chloride, boric oxide, and boron trichloride.[5] Back co-ordination from oxygen to boron is presumably an important factor in carbonium-ion formation, and the greater percentage rearrangement found in decomposition of the dichloroborinates as compared to the chloroboronates, in which back-co-ordination from each individual oxygen atom would be expected to be less, is in accord with this view (Tables 1 and 3). In most cases, the much less stable bromo-esters afforded similar proportions of rearranged products (Table 2). The very slow dealkylation of tri-n-butyl borate with hydrogen chloride or bromide gave only the n-butyl halide.

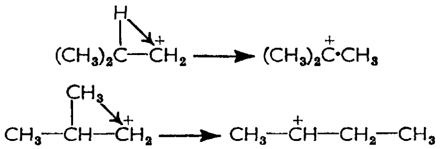
Lewis acids ($AlCl_3$, $FeCl_3$) increased both the rate of decomposition of the chloro-esters and the percentage rearrangement of the alkyl groups;[2] however, boron trichloride strongly suppressed the rate of decomposition, and in the case of n-pentyl dichloroborinate the percentage rearrangement was unaffected.

The overall pattern of rearrangements found (see Tables 1—3) was of n-alkyl groups (Pr^n, Bu^n, n-pentyl, n-octyl) rearranging to s-alkyl groups and of s-alkyl groups rearranging among themselves, *e.g.*:

$$CH_3{\cdot}[CH_2]_6{\cdot}\overset{+}{C}H_2 \longrightarrow CH_3{\cdot}[CH_2]_5{\cdot}\overset{+}{C}H{\cdot}CH_3 \rightleftharpoons CH_3{\cdot}[CH_2]_4{\cdot}\overset{+}{C}H{\cdot}CH_2{\cdot}CH_3 \rightleftharpoons CH_3{\cdot}[CH_2]_3{\cdot}\overset{+}{C}H{\cdot}[CH_2]_2{\cdot}CH_3$$

n-Propyl bromide (*ca.* 8%) was obtained from the interaction of tri-isopropyl borate with boron tribromide, although no n-isomer resulted from the direct interaction of isopropyl alcohol with boron tribromide; also, boron trichloride with tri-isopropyl borate gave no n-propyl chloride. The rearrangement of iso- to n-propyl (1·3%) has been observed, by use of an infrared technique, in the reaction of isopropyl bromide with aluminium bromide,[6] and we have confirmed this rearrangement (2—3%) by gas–liquid chromatography. Although aluminium trichloride caused isopropyl chloride to decompose to hydrogen chloride and polymer, formation of n-propyl chloride was doubtful. s-Butyl chloride [2] and bromide were not isomerised to the n-butyl isomers by the use of the corresponding aluminium halides (Table 4).

In all the straight-chain alkyl systems, only hydrogen migration occurred. The branched isobutyl compounds not only gave t-butyl halide (75%), by hydrogen migration, but 20% or more rearranged to s-butyl by methyl shift. Small amounts (0·02 mol.) of ferric or aluminium chloride increased the total rearrangement to 99% or more, and the proportion of s-halide in the products was increased, in one case to over 50%. Decomposition of di-isobutyl chloroboronte yielded more t-butyl chloride (80%) and less s-alkyl halide (7%), whilst the same catalysts, although accelerating the rate of decomposition, increased the rearrangement to t-butyl halide only slightly and did not significantly affect the yield of s-alkyl halide. s-Butyl alcohol has been found among the products of reaction of isobutylamine with nitrous acid.[7]



Both 1- and 2-phenylethanol reacted with boron trichloride to give the corresponding isomerically pure halides, the former with almost complete loss of rotatory power but

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[4] Linnemann, *Annalen*, 1872, **162**, 24; Whitmore and Langlois, *J. Amer. Chem. Soc.*, 1932, **54**, 3441.

[5] Gerrard and Lappert, *J.*, 1951, 2545; 1955, 3084; Lappert, *J.*, 1956, 1768.

[6] Andreevskii, *Doklady Akad. Nauk. S.S.S.R.*, 1960, **135**, 312.

[7] Cannell and Taft, *J. Amer. Chem. Soc.*, 1956, **78**, 5812.

TABLE 1.

Decomposition of alkyl dichloroborinates, RO·BCl$_2$.

						Alkyl chloride (RCl)			
R	Wt. (g.)	Catalyst (mol.)		Temp.	Time (hr.)	Yield (%)	B. p.	n_D^{20}	Composition (%) R
Pr^n	44·9	—	—	125°	25	54	35—44	1·3842	Pr^n 77; Pr^i 23
,, ...	53·4	FeCl$_3$	0·02	60	2	78	35—48	1·3850	,, 54; ,, 46
,, ...	37·4	AlCl$_3$	0·02	60	5	74	35—47	1·3809	,, 33; ,, 67
Pr^i	58·3 [a]	—	—	20	24	82	35—37	1·3777	,, 0; ,, 100
Bu^n	34·7 [b]	—	—	143	28	92	50—75	—	Bu^n 55; Bu^s 45
Bu^i	57·8	—	—	125	25	67	54—59	1·3880	Bu^t 75; Bu^s >20; Bu^i <5
,, ...	22·5	FeCl$_3$	0·01	20	8	56	54—56	1·3910	,, 48; ,, 52; —
,, ...	31·1	FeCl$_3$	0·02	20	24	66	60—66	1·3875	,, 61; ,, *ca.* 38; Bu^i *ca.* 1
,, ...	30·9	AlCl$_3$	0·02	80	3	49	54—58	1·3879	,, 72; ,, *ca.* 27; ,, *ca.* 1
Bu^t	26·4 [c]	—	—	[d]	—	64	50—53	1·3852	,, 100
n-Pentyl	92·7	—	—	140	25	81	100—106	1·4092	Pe^n 48; Pe^2 31; Pe^3 21
,, ...	48·0	BCl$_3$	0·98	130	22	0 [e]			
,, ...	43·4	,,	1·0	135	21 [f]	52	95—106	1·4087	Pe^n 49; Pe^2 32; Pe^3 19
,, ...	51·1	FeCl$_3$	0·02	100	4	84	95—100	1·4091	,, 55; ,, 27; ,, 18
,, ...	65·8	AlCl$_3$	0·02	100	6	86	94—102	1·4040	,, 38; ,, 39; ,, 23
Me·[CH$_2$]$_2$·CHMe(Pe^2)	37·6 [c]	—	—	20	24	92	93—95	1·4082	,, 0; ,, 63; ,, 37
Et$_2$CH (Pe^3)	33·0	—	—	[d]	—	86	95—98	1·4081	,, 0; ,, 38; ,, 62
n-Octyl	41·5	—	—	195	26	68 [g]	164—182	1·4274	Oc^n 68; Oc^2 25; Oc^3 6; Oc^4 1
Me·[CH$_2$]$_5$·CHMe (Oc^2) [h]	15·1 [c]	—	—	[d]	—	42 [i]	166—168	1·4269	,, 0; ,, 62; ,, 35; ,, 3
,, ...	15·6 [j]	—	—	[d]	—	69 [k]	50—53/10 mm.	1·4266	,, 0; ,, 58; ,, 37; ,, 5
Me·[CH$_2$]$_4$·CHEt (Oc^3)	14·8 [c]	—	—	[d]	—	89	50—53/8 mm.	1·4273	,, 0; ,, 26; ,, 61; ,, 13
Me·[CH$_2$]$_3$·CH·CH$_2$Et (Oc^4) ...	12·8 [c]	—	—	[d]	—	89	62/15 mm.	1·4275	,, 0; ,, 2; ,, 25; ,, 73
Ph·CH$_2$CH$_2$	49·7 [l]	—	—	—	—	93	78/10 mm.	1·5297	Ph·CH$_2$·CH$_2$ 100
Ph·CH·CH$_3$ [m]	2·6 [e]	—	—	[d]	—	73 [n]	86/15 mm.	1·5287	Ph·CH·CH$_3$ 100

[a] From BCl$_3$ (2 mol.) and borate (1 mol.). [b] Pr^{n}Cl (17·8 g.) added, 11·5 g. recovered, no Pr^{i}Cl found. [c] From BCl$_3$ (1 mol.) and the alcohol (1 mol.) at −80°. [d] Unstable, RCl distilled immediately. [e] n-C$_5$H$_{11}$O·BCl$_2$ (43·4 g.) and (n-C$_5$H$_{11}$O)$_2$BCl (2·6 g.) distilled. [f] Then 20° for 72 hr. [g] Plus octene (4·1 g.). [h] From ROH, α_D^{23} +7·97° (l = 1). [i] α_D^{20} +2·31° (l = 1), plus octene (0·5 g.). [j] At −80° from BCl$_3$ (2 mol.) and tri-1-methylheptyl borate (1 mol.), α_D^{26} +29·3° (l = 1) [from ROH α_D^{23} +7·97° (l = 1)]. [k] α_D^{20} +2·36° (l = 1), plus octene (0·25 g.). [l] Undistilled (Found: B, 5·4; Cl, 35·6. Calc. for C$_8$H$_9$BCl$_2$O: B, 5·3; Cl, 34·6%), n_D^{20} 1·5073. [m] α_D^{20} +25·40° (l = 1). [n] α_D^{18} −0·14° (l = 1).

TABLE 2.

Decomposition of alkyl dibromoborinates, RO·BBr$_2$.

Reactants					Alkyl bromide (RBr)			
			BBr$_3$					
R	Alcohol (ROH) or borate [(RO)$_3$B]	Wt. (g.)	(g.)	(mol.)	Yield (%)	B. p.	n_D^{20}	Composition (%) R
Pr^n	Alcohol	5·05	21·1	1·0	77	64—70°	1·4314	Pr^n 72; Pr^i 28
Pr^i	,,	6·0	25·0	1·0	55	57—58	1·4253	,, 0; ,, 100
,, ...	,,	4·5	20·8	1·1	62	59—61	1·4253	,, 0; ,, 100
,, ...	Borate [a]	15·8	44·3	2·1	79	60—62	1·4258	,, 7; ,, 93
,, ...	,,	7·2	20·2	2·1	80	59—62	1·4253	,, 9; ,, 91
Bu^n	Alcohol	7·8	26·4	1·0	90	93—100	1·4379	Bu^n 72; Bu^s 28
,, ...	Borate	11·3	25·2	2·0	91	96—99	1·4384	,, 79; ,, 21

TABLE 2. (*Continued.*)

R	Alcohol (ROH) or borate $[(RO)_3B]$	Wt. (g.)	BBr_3 (g.)	BBr_3 (mol.)	Alkyl bromide (RBr) Yield (%)	B. p.	n_D^{20}	Composition (%) R
Bu^s	Alcohol	7·65	25·4	0·98	81	90°	1·4367	,, 0; ,, 100
Bu^i	,,	8·7	30·8	1·05	80	72—76	1·4301	Bu^t 74; Bu^s *ca.* 21; Bu^i *ca.* 5
n-Pentyl	,,	9·1	25·4	1·1	94	116—122	1·4435	Pe^n 72; Pe^2 16; Pe^3 12
$Me\cdot[CH_2]_2\cdot CHMe$ (Pe^2)	,,	8·7	24·7	1·0	85	112—114	1·4413	,, 0; ,, 88; ,, 12
Et_2CH (Pe^3)	,,	9·0	27·5	1·1	87	112—113	1·4429	,, 0; ,, 43; ,, 57
n-Octyl	,,	12·9	27·3	1·1	97	50—56/0·5 mm.	1·4511	Oc^n 76; Oc^2 14; Oc^3 8; Oc^4 2
$Me\cdot[CH_2]_5\cdot CHMe$ (Oc^2)	,, [b]	7·3	16·3	1·15	88 [c]	60—67/10 mm.	1·4505	,, 0; ,, 45; ,, 36; ,, 19
,,	Borate [d]	7·9	19·4	3·9	90 [e]	50/9 mm.	1·4509	,, 0; ,, 63; ,, 30; ,, 7
$Me\cdot[CH_2]_4\cdot CHEt$ (Oc^3)	Alcohol	7·0	18·5	1·4	77	63—65/7 mm.	1·4515	,, 0; ,, 36; ,, 37; ,, 27
$Me\cdot[CH_2]_3\cdot CH\cdot CH_2\cdot Et$ (Oc^4)	,,	5·4	16·2	1·55	86	80—83/19 mm.	1·4522	,, 0; ,, 8; ,, 28; ,, 64

[a] Hydrolysis gave only isopropyl alcohol. [b] α_D^{23} +7·97° (l = 1). [c] α_D^{20} +0·14° (l = 1). [d] α_D^{26} +29·3° (l = 1) [from ROH, α_D^{23} +7·97° (l = 1)], [e] α_D^{20} +0·30° (l = 1).

TABLE 3.

Decomposition of dialkyl chloroboronates $(RO)_2BCl$.

R	Wt. taken (g.)	Catalyst (g.) *		Temp.	Time (hr.)	Alkyl chloride (RCl) Yield (%)	B. p.	n_D^{20}	Composition (%) R
Bu^n	49·0	—	—	155°	59	37	76—79°	1·4009	Bu^n 85; Bu^s 15
,,	34·8	$FeCl_3$	0·66	20	24	99	72—76	1·3988	,, 65; ,, 32
,,	27·7	$AlCl_3$	0·43	20	3·5	100	72—78	1·3979	,, 42; ,, 58
Bu^s	13·8	—	—	110	8	48 [a]	—	—	,, 0; ,, 100
Bu^i	24·0	—	—	200	27	25	—	1·3879	Bu^t 82; Bu^s *ca.* 7; Bu^i *ca.* 11
,,	27·7	$FeCl_3$	0·59	20	24	82	51—53	1·3860	,, 92; ,, *ca.* 5; ,, *ca.* 3
,,	29·6	$AlCl_3$	0·44	20	24	73	53—58	1·3852	,, 92; ,, *ca.* 6; ,, *ca.* 2
Bu^t	20·8 [b]	—	—	—	—	97	48·5	1·3834	,, 100

* 0·02 mol.

[a] *cis*- and *trans*-But-2-ene (1·9 g., 0·48 mol.) also obtained (infrared). [b] From BCl_3 (13·0 g.) and Bu^tOH (16·0 g., 1·95 mol.) in ether (4·9 g.) at −80°, decomposed spontaneously at 20°.

TABLE 4.

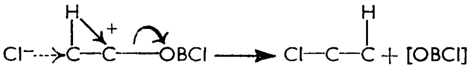
Isomerisation of alkyl halides.

Alkyl halide	Wt. taken (g.)	Catalyst	Catalyst (g.)	Catalyst (mol.)	Temp.	Time (hr.)	Alkyl halide isolated Yield [a] (%)	B. p.	n_D^{20}	Composition (%) R
Pr^iCl	16·5	$AlCl_3$	0·8	0·03	36°	11	76	37—38°	1·3773	Pr^i *ca.* 100 [b]
Pr^iBr	31·3	$AlBr_3$	1·6	0·02 [c]	60	6	96	59—60	1·4238	Pr^i 98; Pr^n 2
,,	9·3	,,	2·1	0·10	20	24	62	59—60	1·4248	,, 97; ,, 3
Bu^nCl	38·2	$AlCl_3$	1·11	0·02	78	2·5	71	68—79	1·4012	Bu^n 91; Bu^s 9
Bu^sBr	14·3	$AlBr_3$	0·74	0·03	90	6	92	89—91	1·4368	Bu^s 100

[a] In all experiments, hydrogen halide was evolved and a brown polymer remained. [b] Trace Pr^nCl suspected (g.l.c.), but too small to confirm by infrared spectroscopy. [c] Water (0·1 g.) added.

with slightly preponderant inversion of configuration. The deamination of [1-^{14}]-2-phenylethylamine gave 2-phenylethanol, although some isotope position interchange of the ethyl carbon atoms was observed.[8]

Rearrangement by a remote S_N2 process (1) is a possibility, and an S_Ni mechanism, which would not lead to rearrangement, could account for some loss in optical purity.



(1)

Rearrangement occurs mainly, if not entirely, during formation of the alkyl halide. Thus, when n-butyl dichloroborinate was thermally decomposed in the presence of n-propyl chloride, the latter was unaffected.

EXPERIMENTAL

Gas-chromatographic and infrared spectroscopic analyses were used to check the purity of the starting alcohols and to analyse the alkyl halide products.[1]

The esters [2,5,9] were attested by chemical analysis and physical constants. *n-Pentyl dichloroborinate* (87% yield) had b. p. 46°/12 mm., n_D^{20} 1·4178 (Found: B, 6·7; Cl, 41·8. $C_5H_{11}BCl_2O$ requires B, 6·4; Cl, 42·1%). Decomposition of the esters, and isolation of the alkyl halides produced, were as described earlier for n-butyl dichloroborinate.[2] The less-stable compounds (including all the bromo-esters) were prepared by mixing the appropriate proportions of reagents (−80°), and were then allowed to decompose at room temperature before distillation. Results are shown in Tables 1—3.

Reaction of Tri-n-butyl Borate with Hydrogen Chloride.—No butyl chloride was formed when hydrogen chloride, in excess, was passed into the borate at 170—180° (25 hr.). The borate (31·8 g.) with hydrogen chloride (7·13 g., 1·42 mol.) (absorbed at −80°) was heated at 100° in a sealed tube (120 hr.). Boric acid (3·0 g., 0·35 mol.) was precipitated, and the liquid gave n-butyl chloride (0·84 mol.), b. p. 77°, n_D^{20} 1·4011 (Found: Cl, 38·7. Calc. for C_4H_9Cl: Cl, 38·4%), an aqueous layer (1·09 g.), tri-n-butyl borate (0·6 mol.), b. p. 111—116°/13 mm., n_D^{20} 1·4085 (Found: B, 4·8. Calc. for $C_{12}H_{29}BO_3$: B, 4·7%), and a dark viscous residue (2·63 g.) (Found: B, 15·2%).

Reaction of Tri-n-butyl Borate with Hydrogen Bromide.—Hydrogen bromide, in excess, was passed into the borate (49·7 g., 1 mol.) at 100—120° (14 hr.). Water (1·2 g.), n-butyl bromide (0·89 mol.), b. p. 98·5—100°, n_D^{21} 1·4367 (Found: Br, 57·9. Calc. for C_4H_9Br: Br, 58·3%), n-butanol (2·9 g.) (infrared), tri-n-butyl borate (0·2 mol), b. p. 104—105°/10 mm., n_D^{20} 1·4095 (Found: B, 4·9%), and a solid residue (3·8 g.) (Found: B, 30·1. Calc. for B_2O_3: B, 31·1%) were obtained.

Isomerisation of Alkyl Halides.—Aluminium trichloride or tribromide was added to the alkyl halide at 20° and the mixture was heated under reflux (see Table 4). The products were distilled for analysis.

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[8] Roberts and Regan, *J. Amer. Chem. Soc.*, 1953, **75**, 2069.
[9] Gerrard and Lappert, *J.*, 1951, 1020.