

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

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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

¹ Part II, Gerrard and Hudson, preceding Paper.

² Gerrard, Hudson, and Murphy, *J.*, 1962, 1099.

³ Baddeley, *Quart. Rev.*, 1954, **8**, 355.

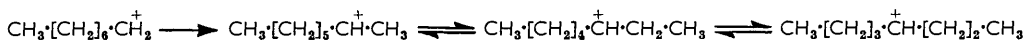
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reaction shown to afford rearrangement from an n- and to an s-alkyl group is that of primary amines with nitrous acid.⁴

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.

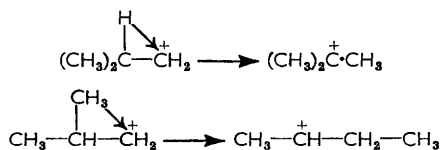
Lewis acids (AlCl_3 , FeCl_3) increased both the rate of decomposition of the chloro-esters and the percentage rearrangement of the alkyl groups;² however, boron trichloride strongly suppressed the rate of decomposition, and in the case of n-pentyl dichloroborinate the percentage rearrangement was unaffected.

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.:



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 chloride² 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 chloroborate 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

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.

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TABLE 1.
Decomposition of alkyl dichloroborinates, RO·BCl₂.

R	Wt. (g.)	Catalyst (mol.)	Temp.	Time (hr.)	Yield (%)	Alkyl chloride (RCl)	
						B. p.	Composition (%) R
Pr ^a	44.9	—	125°	25	54	n _D ²⁰ 1.3842	Pr ^a 77; Pr ^l 23
"	53.4	FeCl ₃	60	2	78	1.3850	" 54; " 46
"	37.4	AlCl ₃	60	5	74	1.3809	" 33; " 67
Pr ^l	58.3 ^a	—	20	24	82	1.3777	" 0; " 100
Bu ^a	34.7 ^b	—	143	28	92	—	Bu ^a 55; Bu ^l 45
Bu ^l	57.8	—	125	25	67	1.3880	Bu ^l 75; Bu ^s >20; Bu ^l <5
"	22.5	FeCl ₃	20	8	56	1.3910	" 48; " 52
"	31.1	FeCl ₃	20	24	66	1.3875	" 61; " ca. 38; Bu ^l ca. 1
"	30.9	AlCl ₃	80	3	49	1.3879	" 72; " ca. 27; " ca. 1
Bu ^l	26.4 ^c	—	4 ^d	—	64	1.3852	" 100
n-Pentyl	92.7	—	140	25	81	1.4092	Pe ^a 48; Pe ^s 31; Pe ³ 21
"	48.0	BCl ₃	130	22	0 ^e	—	—
"	43.4	—	135	21 ^f	52	1.4087	Pe ^a 49; Pe ^s 32; Pe ³ 19
"	51.1	FeCl ₃	100	4	84	1.4091	" 55; " 27; " 18
"	65.8	AlCl ₃	100	6	86	1.4040	" 38; " 39; " 23
Me ^l [CH ₂] ₄ ·CHMe(Pe ^s)	37.6 ^e	—	20	24	92	1.4082	" 0; " 63; " 37
Et ₂ CH (Pe ^s)	33.0	—	195	26	86	1.4081	" 0; " 38; " 62
n-Octyl	41.5	—	4 ^d	—	68 ^g	1.4274	Oc ^a 68; Oc ^s 28; Oc ³ 6
Me ^l [CH ₂] ₅ ·CHMe (Oc ^s) ^h	15.1 ^e	—	4 ^d	—	42 ⁱ	1.4269	" 0; " 62; " 35; " 3
Me ^l [CH ₂] ₄ ·CHEt (Oc ^s)	15.6 ^j	—	4 ^d	—	69 ^k	1.4266	" 0; " 58; " 37; " 5
Me ^l [CH ₂] ₃ ·CHEt (Oc ^s)	14.8 ^c	—	4 ^d	—	89	1.4273	" 0; " 26; " 61; " 13
Me ^l [CH ₂] ₃ ·CH·CH ₂ Et (Oc ^s)	12.8 ^c	—	4 ^d	—	89	1.4275	" 0; " 2; " 73
Ph·CH ₂ CH ₂	49.7 ^l	—	—	—	93	1.5297	Ph·CH ₂ ·CH ₂ 100
Ph·CH·CH ₂ ^m	2.6 ^e	—	4 ^d	—	73 ⁿ	1.5287	Ph·CH·CH ₂ 100

^a From BCl₃ (2 mol.) and borate (1 mol.). ^b Pr·Cl (17.8 g.) added, 11.5 g. recovered, no Pr·Cl found. ^c From BCl₃ (1 mol.) and the alcohol (1 mol.) at -80°. ^d Unstable, RCl distilled immediately. ^e n-C₈H₁₇O·BCl₂ (43.4 g.) and (n-C₈H₁₇O)₂BCl (2.6 g.) distilled. ^f Then 20° for 72 hr. ^g Plus octene (4.1 g.). ^h From ROH, α_D²⁰ +7.97° (l = 1). ⁱ α_D²⁰ +2.31° (l = 1), plus octene (0.5 g.). ^j At -80° from BCl₃ (2 mol.) and tri-1-methylheptyl borate (1 mol.), α_D³⁶ +29.3° (l = 1) [from ROH α_D²³ +7.97° (l = 1)]. ^k α_D²⁰ +2.36° (l = 1), plus octene (0.25 g.). ^l Undistilled (Found: B, 5.4; Cl, 35.6. Calc. for C₈H₁₇BCl₂O: B, 5.3; Cl, 34.6%). ^m α_D²⁰ +25.40° (l = 1). ⁿ α_D¹⁸ -0.14° (l = 1).

TABLE 2.

Decomposition of alkyl dibromoborinates, RO·BBr₂.

R	Alcohol (ROH) or borate [(RO) ₃ B]	Reactants		BBr ₂		Yield (%)		Alkyl bromide (RBr)		Composition (%) R	
		Wt. (g.)	(g.)	(g.)	(mol.)	B. p.	n _D ²⁰	Pr ^a	Pr ^l	Bu ^a	Bu ^l
Pr ^a	Alcohol	5.05	21.1	21.1	1.0	64-70°	1.4314	Pr ^a 72; Pr ^l 28			
Pr ^l	"	5.05	21.1	6.0	1.0	57-58	1.4253	" 0; " 100			
"	"	4.5	20.8	20.8	1.1	59-61	1.4253	" 0; " 100			
"	Borate ^a	15.8	44.3	44.3	2.1	60-62	1.4258	" 7; " 93			
"	"	7.2	20.2	20.2	2.1	59-62	1.4253	" 9; " 91			
Bu ^a	Alcohol	7.8	26.4	26.4	1.0	93-100	1.4379	Bu ^a 72; Bu ^l 28			
"	Borate	11.3	25.2	25.2	2.0	96-99	1.4384	" 79; " 21			

TABLE 2. (Continued.)

R	Alcohol (ROH) or borate [(RO) ₂ B]		Wt. (g.)	BBr ₃		Yield (%)	Alkyl bromide (RBr)		Composition (%) R
	(g.)	(mol.)		B. p.	<i>n</i> _D ²⁰				
Bu ^a	7-65	25.4	0.98	81	90°	1.4367	0;	100	
Bu ^b	8-7	30.8	1.05	80	72-76	1.4301	Bu ^a 74; Bu ^b ca. 21; Bu ^c ca. 5		
n-Pentyl	9-1	25.4	1.1	94	116-122	1.4435	Pe ^a 72; Pe ^b 16; Pe ^c 12		
Me-[CH ₂] ₂ -CHMe (Pe ^a)	8-7	24.7	1.0	85	112-114	1.4413	0;	88;	
Et ₂ CH (Pe ^b)	9-0	27.5	1.1	87	112-113	1.4429	0;	43;	
n-Octyl	12-9	27.3	1.1	97	50-56/0.5 mm.	1.4511	Oc ^a 76; Oc ^b 14; Oc ^c 8; Oc ^d 2		
Me-[CH ₂] ₅ -CHMe (Oc ^a)	7-3	16.3	1.15	88 ^c	60-67/10 mm.	1.4505	0;	45;	
Borate ^d	7-9	19.4	3.9	90 ^e	50/9 mm.	1.4509	0;	63;	
Me-[CH ₂] ₄ -CHEt (Oc ^b)	7-0	18.5	1.4	77	63-65/7 mm.	1.4515	0;	36;	
Me-[CH ₂] ₃ -CH-CH ₂ -Et (Oc ^c)	5-4	16.2	1.55	86	80-83/19 mm.	1.4522	0;	8;	
							0;	28;	

^a Hydrolysis gave only isopropyl alcohol. ^b $\alpha_D^{23} + 0.14^\circ$ ($l = 1$). ^c $\alpha_D^{20} + 29.3^\circ$ ($l = 1$). ^d $\alpha_D^{26} + 29.3^\circ$ ($l = 1$) [from ROH, $\alpha_D^{23} + 7.97^\circ$ ($l = 1$)], ^e $\alpha_D^{20} + 0.30^\circ$ ($l = 1$).

TABLE 3.

Decomposition of dialkyl chloroborates (RO)₂BCl.

R	Wt. taken (g.)	Catalyst (g.) ^a	Temp.	Time (hr.)	Yield (%)	Alkyl chloride (RCI)		Composition (%) R
						B. p.	<i>n</i> _D ²⁰	
Bu ^a	49.0	—	155°	59	37	1.4009	Bu ^a 85; Bu ^b 15	
"	34.8	FeCl ₃	20	24	99	72-76	1.3988	65; "
"	27.7	AlCl ₃	20	3-5	100	72-78	1.3979	42; "
Bu ^b	13.8	—	110	8	48 ^a	—	0;	58
Bu ^c	24.0	—	200	27	25	1.3879	Bu ^b 82; Bu ^c ca. 7; Bu ^d ca. 11	
"	27.7	FeCl ₃	20	24	82	51-63	1.3860	92; "
"	29.6	AlCl ₃	20	24	73	53-58	1.3852	ca. 5; "
Bu ^d	20.8 ^b	—	—	—	97	48.5	1.3834	ca. 6; "

* 0.02 mol.

^a *cis*- and *trans*-But-2-ene (1.9 g., 0.48 mol.) also obtained (infrared). ^b From BCl₃ (13.0 g.) and Bu^cOH (16.0 g., 1.95 mol.) in ether (4.9 g.) at -80° , decomposed spontaneously at 20° .

TABLE 4.

Isomerisation of alkyl halides.

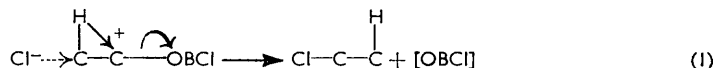
Alkyl halide	Wt. taken (g.)	Catalyst		Temp.	Time (hr.)	Yield ^a (%)	Alkyl halide isolated		Composition (%) R
		(g.)	(mol.)						
Pr-Cl	16.5	AlCl ₃	0.8	36°	11	76	B. p.	<i>n</i> _D ²⁰	Pr ¹ ca. 100 ^b
Pr-Br	31.3	AlBr ₃	1.6	0-02 ^c	6	96	37-38°	1.3773	Pr ¹ 98; Pr ² 2
"	9.3	"	2.1	0.10	20	62	59-60	1.4238	Pr ¹ 98; Pr ² 2
Bu ^a -Cl	38.2	AlCl ₃	1.11	0-02	2.5	71	59-60	1.4248	Bu ^a 91; Bu ^b 9
Bu ^b -Br	14.3	AlBr ₃	0.74	0-03	6	92	68-79	1.4012	Bu ^a 97; Bu ^b 9
						92	89-91	1.4368	Bu ^a 100

^a In all experiments, hydrogen halide was evolved and a brown polymer remained. ^b Trace Pr-Cl suspected (g.l.c.), but too small to confirm by infra-red spectroscopy. ^c Water (0.1 g.) added.

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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.



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*_D²⁰ 1.4178 (Found: B, 6.7; Cl, 41.8. C₅H₁₁BCl₂O 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*_D²⁰ 1.4011 (Found: Cl, 38.7. Calc. for C₄H₉Cl: Cl, 38.4%), an aqueous layer (1.09 g.), tri-n-butyl borate (0.6 mol.), b. p. 111—116°/13 mm., *n*_D²⁰ 1.4085 (Found: B, 4.8. Calc. for C₁₂H₂₆BO₃: 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*_D²¹ 1.4367 (Found: Br, 57.9. Calc. for C₄H₉Br: Br, 58.3%), n-butanol (2.9 g.) (infrared), tri-n-butyl borate (0.2 mol), b. p. 104—105°/10 mm., *n*_D²⁰ 1.4095 (Found: B, 4.9%), and a solid residue (3.8 g.) (Found: B, 30.1. Calc. for B₂O₃: 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.