

204. *s*-Butyl Chloride from *n*-Butyl Dichloroborinate and from *n*-Butanol-Hydrogen Chloride.

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

Formation of *s*-butyl chloride in certain *n*-butyl systems is illustrated by reference to the decomposition of *n*-butyl dichloroborinate, alone and in the presence of catalysts; also by the interaction of butan-1-ol with hydrogen chloride in presence of zinc chloride.

DURING a study¹ of the interaction of the ester of one non-metal with the halide of another (B, Si, P, S, or Ti) it became evident that the alkyl halide produced in *n*-alkyl systems was not always the pure *n*-isomer. Decomposition of *n*-butyl dichloroborinate has been reported;^{2,3} but application of vapour-phase chromatography and infrared spectroscopy has now shown that considerable rearrangement can occur.

Whereas *n*-butyl dichloroborinate slowly gives a mixture of *n*- and *s*-butyl chlorides at 150°, addition of traces of aluminium chloride or ferric chloride causes violent

Decomposition of BuⁿOBCl₂.

Expt. no.	Wt. taken (g.)	Catalyst	(g.)	(mol.)	Temp. (°c.)	Time of heating (hr.)
1	19.0	None	—	—	150	2.5
2	38.0	None	—	—	150	22.5
3	43.4	TiCl ₄	53.1	1.0	150	2.0
4	33.4	FeCl ₃	0.70	0.02	20—80	2.0
5	45.7	AlCl ₃	0.79	0.02	20—80	3.5
6	14.7	BCl ₃	11.9	1.0	85	2.0
7	29.4	BCl ₃	21.3	1.0	130	22.0

Expt. No.	Crude BuCl isolated		Distilled BuCl					
	(g.)	(mol.)	Yield (g.)	(mol.)	Cl (%)	B. p.	n_D^{20}	Composition (%) Bu ⁿ Cl Bu ^s Cl
1	6.2	0.55	4.2	0.37	—	66—76°	1.3985	75 25
2	15.9	0.70	14.2	0.63	—	68—77	1.4005	76 24
3	18.4	0.71	15.8	0.61	38.4	66—73	1.3989	42 58
4	13.6	0.68	11.9	0.59	—	66—74	1.3984	37 63
5	23.0	0.84	18.0	0.66	39.4	68—74	1.3975	21 79
6	Bu ⁿ OBCl ₂ (12.0 g., 82%), b. p. 30°/16 mm. (Found: B, 6.8; Cl, 44.3%) *							
7	Bu ⁿ OBCl ₂ (14.7 g., 50%) (Found: B, 7.2; Cl, 44.5%) and mainly (Bu ⁿ O) ₂ BCl (8.2 g., 45%) (Found: B, 6.2; Cl, 18.1%) †							

* Calc. for C₄H₉BCl₂O: B, 7.0; Cl, 45.8%. † Calc. for C₈H₁₇BClO₂: B, 5.6; Cl, 18.4%.

decomposition at room temperature, and considerable increase in formation of *s*-butyl chloride. Titanium tetrachloride is less effective, whilst boron trichloride suppresses alkyl halide formation (see Table). These results are in accord with rearrangement in



an intermediate carbon cation consequent on an S_N1 mechanism. A similar rearrangement is evident in the solvolysis of *n*-propyl bromide,⁴ and in the dehydration of butan-1-ol.⁵ Isomerisation of the alkyl halide after formation by a Friedel-Crafts catalyst⁶

¹ Gerrard and Griffey, *J.*, 1960, 3170; 1961, 4095; Frazer, Gerrard, and Singh, *J.*, 1961, 4680; Cooper and Gerrard, *Chem. and Ind.*, 1961, 320.

² Gerrard and Lappert, *J.*, 1951, 1020, 2545.

³ Gerrard and Lappert, *Chem. Rev.*, 1958, 58, 1087.

⁴ Coe and Gold, *J.*, 1960, 4940.

⁵ Whitmore, *J. Amer. Chem. Soc.*, 1932, 54, 3279.

⁶ Baddeley, *Quart. Rev.*, 1954, 8, 355; R. M. Roberts and Panayides, *J. Org. Chem.*, 1958, 23, 1080; J. D. Roberts, McMahon, and Hine, *J. Amer. Chem. Soc.*, 1949, 71, 1896; 1950, 72, 4237.

would not account for the proportion of *s*-butyl chloride in our products. The rearrangement of the *n*-butyl cation is probably not reversible, as the thermal decomposition of *s*-butyl dichloroborinate gave exclusively *s*-butyl chloride, and the latter was not isomerised by aluminium trichloride.

In searching for pure specimens of *n*-butyl chloride for analytical purposes we found that most commercial products contained the *s*-isomer (in some cases as much as 15%), and have therefore made a preliminary investigation of the hydrogen chloride-alcohol system in respect of its efficiency for the preparation of isomerically pure alkyl chlorides. Interaction of hydrogen chloride and butan-1-ol at the b. p. was slow but gave exclusively *n*-butyl chloride. At 160° in a sealed tube the reaction was much quicker, and no more than a trace of *s*-butyl chloride was formed. Zinc chloride⁷ has long been used as a catalyst in these systems, and we found that in its presence at room temperature the initial product was *n*-butyl chloride. As the reaction proceeded the product contained a progressively larger proportion of *s*-butyl chloride and preparation in a sealed tube at 160° gave a product containing over 20% of *s*-butyl chloride. Zinc chloride caused no isomerisation of *n*-butyl chloride under reflux.

EXPERIMENTAL

Butan-1-ol was attested by infrared spectroscopy and gas-liquid chromatography and was used to prepare *n*-butyl dichloroborinate,² b. p. 30°/15 mm. (Found: B, 7.1; Cl, 45.5. Calc. for $C_4H_9BCl_2O$: B, 7.0; Cl, 45.8%). Alkali-hydrolysis of the ester afforded only butan-1-ol.

Butan-1-ol was separable from other isomers by gas-liquid chromatography on a 30% liquid paraffin-Celite column and was also shown to be pure by the infrared spectrum.

Mixtures of *n*-butyl and *s*-butyl chloride were characterised by infrared spectra, which showed bands at 747, 728, 652 cm^{-1} (Bu^n) and 794, 669, 628, 609 cm^{-1} (Bu^s), but not at 685 cm^{-1} (Bu^i) or 570 cm^{-1} (Bu^t), and by gas-liquid chromatography on a 30% squalane-Celite column with which quantitative analyses were made.

Decomposition of n-Butyl Dichloroborinate.—Separate quantities of the compound were heated, alone or with added titanium tetrachloride, boron trichloride being allowed to escape to a trap (−80°). The butyl chlorides were then distilled, washed with water, dried (K_2CO_3), and redistilled, giving a wide-boiling fraction (*e.g.*, 66–76°), which was analysed, and distilled to yield arbitrarily chosen fractions to be separately analysed.

Each drop of the dichloroborinate added to the anhydrous chloride (Al, Fe) (0.02 mol.) at room temperature reacted violently. Addition time was 2 hr. Butyl chlorides were allowed to distil to a receiver (−80°) as they were formed, and the residue was finally heated to 80°. The product was washed, dried, distilled, and analysed, as already stated.

Samples of the dichloroborinate and boron trichloride were heated under reflux in an apparatus fitted with a "Drikold" condenser (−80°). No butyl chloride could afterwards be isolated, and there was a high recovery of dichloroborinate (with some di-*n*-butyl chloroborate from the higher temperature reaction).

Decomposition of s-Butyl Dichloroborinate.—The unstable dichloroborinate² was prepared at −80° from butan-2-ol (26.7 g., 1 mol.) and boron trichloride (42.1 g., 1 mol.). Distillation gave a product which was washed, dried, and redistilled, affording pure *s*-butyl chloride (30.4 g., 0.9 mol.), b. p. 67.5–68.5°, n_D^{20} 1.3965 (Found: Cl, 38.2. Calc. for C_4H_9Cl : Cl, 38.4%). Gas-liquid chromatography showed no trace of *n*-butyl chloride.

Reaction of Butan-1-ol with Hydrogen Chloride.—Anhydrous hydrogen chloride was passed into butan-1-ol (90.8 g.) under reflux (118°) in a flask fitted with a fractionating column. Distillate was slowly removed (5 hr.), so that the head temperature did not exceed 85°. The upper layer (5.2 g.) was washed and dried, giving *n*-butyl chloride (3.7 g., 3.3%), n_D^{20} 1.4018, b. p. 79–80° (Found: Cl, 38.2%).

Similarly, butan-1-ol (64.9 g.) containing zinc chloride (24.5 g., 0.2 mol.) gave butyl chloride quickly. Fractions were collected between 60° and 80° during four 30-min. intervals, and were washed and dried, giving (i) 12.3 g., n_D^{20} 1.4020 (Bu^nCl , 100), (ii) 24.1 g., n_D^{20} 1.4012 (Bu^nCl , 98.4; Bu^sCl , 1.6), (iii) 7.9 g., n_D^{20} 1.4002 (Bu^nCl , 97.6; Bu^sCl , 2.4), and (iv) 6.8 g., n_D^{20} 1.3988 (Bu^nCl , 95.7; Bu^sCl , 4.3%) (total yield, 63%).

⁷ Groves, *J.*, 1874, **12**, 636; Norris and Taylor, *J. Amer. Chem. Soc.*, 1924, **46**, 753.

In a sealed tube at 160° (10 hr.), butan-1-ol (4.1 g.) and hydrogen chloride (1.76 g., 0.87 mol.) gave water (1.0 g.) and an organic layer (4.87 g.) which, after drying, gave a fraction (3.5 g.), b. p. 78.5–81°, n_D^{21} 1.4010 (Found: Cl, 37.0%), another (0.5 g.), b. p. 81–86°, n_D^{21} 1.4010 (Found: Cl, 34.5%), and a residue (0.07 g.), n_D^{20} 1.4020. A cold trap (–80°) received a trace of olefin. The butyl chloride (0.75 mol.) contained <1% of s-butyl chloride.

Similarly, at 160° (10 hr.), butan-1-ol (10.3 g.), zinc chloride (3.9 g., 0.2 mol.), and hydrogen chloride (3.0 g., 0.6 mol.) afforded a product which gave fractions (i) 3.4 g., b. p. 75–81°, n_D^{20} 1.4009 (Found: Cl, 36.6%), and (ii) 1.1 g., b. p. 81–140°, n_D^{20} 1.4025 (Found: Cl, 33.2%). Olefin was also formed. The average composition of the total butyl chloride (0.33 mol.) was BuⁿCl 79% and Bu^sCl 21%.

Isomerisation of n-Butyl Chloride.—Aluminium trichloride (1.0 g., 0.02 mol) was added to n-butyl chloride (34.7 g., 1 mol.) at room temperature. After being heated for 2.5 hr. at reflux temperature a sample contained BuⁿCl 97.5% and Bu^sCl 2.5%, this composition being virtually unchanged after 13 hours' heating. Addition of more aluminium trichloride (0.75 g.) to the remainder (27.0 g.) caused further isomerisation to give BuⁿCl 90%, Bu^sCl 10%, which became BuⁿCl 88.5%, Bu^sCl, 11.5%, after 3 hours' further heating. Distillation then gave a mixture (13.4 g.) (Found: Cl, 38.0%), b. p. 76°, $n_D^{20.5}$ 1.4007, containing BuⁿCl 88% and Bu^sCl 12%. Hydrogen chloride (1.28 g.; equivalent to 1.96 g. of butene) was collected in potassium hydroxide, and the residue was polymeric.

n-Butyl chloride (18.3 g.) was heated under reflux for 6 hr. with boron trichloride (23.1 g., 1 mol.). Next morning distillation gave n-butyl chloride (18.5 g.) (Found: Cl, 38.2%), b. p. 75.5–77°, n_D^{20} 1.4017, and no detectable s-isomer.

Similarly, n-butyl chloride (32.1 g.) was heated under reflux (24 hr.) with anhydrous zinc chloride (12.9 g., 1 mol.). No change in still-head temperature was noted, and the first 5 ml. of distillate was shown to be the n-isomer, b. p. 78°, n_D^{20} 1.4019.

Effect of Aluminium Trichloride on s-Butyl Chloride.—s-Butyl chloride (27.3 g.) and aluminium trichloride (0.8 g., 0.02 mol) were heated under reflux for 6 hr. s-Butyl chloride (18.0 g.) (Found: Cl, 38.3%), b. p. 68.5°, n_D^{20} 1.3958, and hydrogen chloride (1.2 g.) equivalent to butene (1.8 g.) were obtained. There was a residue (5.2 g.) which at 80°/15 mm. gave a mixture (2.9 g.) of s-butyl chloride, small amounts of unidentified compounds (possibly hydrocarbons), and a polymeric residue.

We thank Dr. E. F. Mooney and Mr. M. Goldstein for the infrared measurements.

NORTHERN POLYTECHNIC,
HOLLOWAY ROAD, LONDON, N.7.

[Received, July 13th, 1961.]