Intervention of Polyhalides in Thionyl Bromide–Alcohol Systems.

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Thionyl bromide and pyridinium bromide readily form pyridinium tribromide which functions as bromine and pyridinium bromide, whereas pyridinium trichloride has not been obtained from corresponding reagents. Therefore, in thionyl bromide–alcohol–pyridine systems complications arise which have not been discerned in thionyl chloride ones. Intervention of tribromide ion leads to reduced yields and rotatory power of alkyl bromide, and to halogenation of a double bond in the alcohol. These complications are largely avoided by using thionyl bromide, a trace of pyridinium bromide, and previously formed sulphite. Experiments with other trihalide ions are described.

Interaction of thionyl chloride and an alcohol of ordinary reactivity (such as *n*-butanol) includes the sequence of reactions (1)—(4) (see Gerrard, Machell, and Tolcher, *Research*, 1955, **8**, S7; Gerrard and Schild, *Chem. and Ind.*, 1954, 1232). In the presence of pyridine, the base hydrochloride formed during reactions (1) and (2) powerfully accelerates (3) and rather less effectively (4). Intervention by pyridinium trichloride, $C_5H_5NHCl_3$, has not been discerned; for, although there is evidence that the trichloride can exist, it is probably not formed by the interaction of thionyl chloride and pyridinium chloride (Frazer and Gerrard, *Research*, 1954, **7**, S27). On the other hand, pyridinium tribromide is readily formed during the addition of thionyl bromide to base hydrobromide, and its intervention weakens the analogy between the thionyl bromide and the thionyl chloride system.

$$\mathrm{BuOH + SOCl_2 \xrightarrow{quick} BuO{\cdot}SOCl + HCl} \quad . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$\mathrm{BuOH + BuO{\cdot}SOCl \xrightarrow{quick} (BuO)_2SO + HCl} \quad . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$\mathrm{(BuO)_2SO + SOCl_2 \xrightarrow{slow} 2BuO{\cdot}SOCl} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

$$\mathrm{BuO{\cdot}SOCl \xrightarrow{slow} BuCl + SO_2} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

Other trihalides, *e.g.*, Cl_2Br^-, Br_2Cl^-, Cl_2I^-, Br_2I^-, are obtained from pyridinium halide and the appropriate thionyl halide (5), and in Table 2 are recorded results of the interaction

$$\mathrm{2SOX_2 + 2C_5H_5NHY \longrightarrow 2C_5H_5NHX_2Y + S + SO_2} \quad . \; . \; . \; . \; . \quad (5)$$

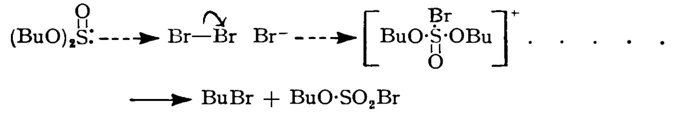
of these trihalides with di-*n*-butyl sulphite. Trihalides can function as a monohalide and halogen or interhalogen compound, the smaller halogen remaining as the base hydrohalide. Thus the trihalide $C_5H_5NHClBr_2$ functions as bromine and the hydrochloride, and $C_5H_5NHCl_2Br$ as bromine chloride and hydrochloride. If we assume analogy with chlorine (Levaillant, *Ann. Chim.*, 1936, **6**, 461; Gerrard, *J.*, 1940, 218; Cross and Gerrard, *J.*, 1949, 2686) bromine should react according to (6), and bromine chloride to (7).

TABLE 1.

Pyridinium polyhalide	Method †	Yield (%)	M. p.	Colour	Halogen (equiv./mole): total	available	Found (%): C	H	Calc. (%): C	H
Cl_3 *	*a*	91	50—55°	Light yellow	2·45	1·56	—	—	—	—
$BrCl_2$	*b*	93	136—137	Yellow	2·92	1·97	27·1	2·6	26·0	2·6
Br_2Cl * ...	*c*	59	94—96	Orange	3·00	1·99	23·7	2·4	21·8	2·2
Br_3	*c*	75	135	Red	2·95	1·89	24·0	1·8	24·7	1·9
Cl_2I	*d*	78	187	Yellow	2·72	2·03	21·9	2·5	21·6	2·2
Br_2I	*d*	84	176—177	Brown	2·91	1·91	16·7	1·8	16·4	1·65
ClI_2 *	*e*	68	65—70	Black	2·92 *f*	2·14	17·1	1·9	16·2	1·6
BrI_2 * ...	*e*	64	139—141	Black	2·82 *f*	1·86	15·2	1·0	14·5	1·5

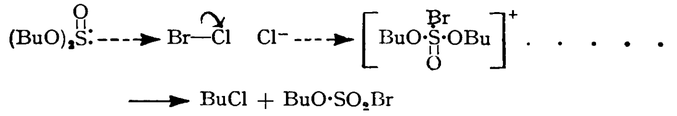
* New compounds.

† (*a*) Liquid chlorine (26·0 g., 2 mol.) was added to pyridine hydrochloride (22·0 g., 1 mol.) at −80° During 0·5 hr. at 20° chlorine (16·0 g., 1·2 mol.) was lost, leaving a light yellow solid (32·0 g.), but there was no further loss in weight when the product, protected by a calcium chloride tube, was left open to the atmosphere for 18 hr. at 20°. However, attempts to recrystallise the solid led to its decomposition, and loss of chlorine. (*b*) Chlorine was passed through a suspension of pyridine hydrobromide in carbon tetrachloride and chloroform. (*c*) Bromine was added to the hydrochloride or hydrobromide. (*d*) These compounds were prepared from the appropriate thionyl halide (Frazer and Gerrard, *Research*, 1954, **7**, S27). (*e*) Iodine and the hydrochloride or hydrobromide were mixed in glacial acetic acid. (*f*) To obtain these figures it was found necessary to reduce the compound as follows. Sulphur dioxide was passed (5 min.) through a warm alcoholic solution of a sample of the compound, and total halogen was then determined by a Volhard titration.



$$\mathrm{(BuO)_2\overset{O}{\overset{\|}{S}}\!: \dashrightarrow \overset{\curvearrowright}{Br{-}Br}\;\; Br^- \dashrightarrow \left[BuO{\cdot}\underset{\underset{O}{\|}}{\overset{Br}{S}}{\cdot}OBu\right]^+} \quad . \; . \; . \; . \; . \; . \quad (6)$$

$$\mathrm{\longrightarrow BuBr + BuO{\cdot}SO_2Br}$$



$$\mathrm{(BuO)_2\overset{O}{\overset{\|}{S}}\!: \dashrightarrow \overset{\curvearrowright}{Br{-}Cl}\;\; Cl^- \dashrightarrow \left[BuO{\cdot}\underset{\underset{O}{\|}}{\overset{Br}{S}}{\cdot}OBu\right]^+} \quad . \; . \; . \; . \; . \; . \quad (7)$$

$$\mathrm{\longrightarrow BuCl + BuO{\cdot}SO_2Br}$$

In the example of the dibromochloride, alkyl chloride can still be formed, because chloride ions from the base hydrochloride can compete with bromide ions during the second stage of the sequence of reactions. From the nature of chlorosulphonates (see Levaillant; and Cross and Gerrard, *locc. cit.*), it may be expected that bromosulphonates will tend to give alkyl bromide and consequently a mixture of alkyl halides results when the dichlorobromide is used. It is noticeable that trihalides containing iodine react much more slowly, and although this may be partly due to their known stability in dissociating conditions, it is probable that iodine halide reacts much more slowly with the sulphite.

TABLE 2.

Pyridinium polyhalide	g.	$(RO)_2SO$ g. (1 mol.)	Time (hr.)	Temp.	Method	Alkyl halide				RCl (mol.)	RBr (mol.)	2nd Fraction (g.)	Solid residue (g.)
						g.	b. p.	n_D^{20}	d_4^{20}				
Cl_3	12·70	13·00	50	20°	*A*	7·30	78—79°	1·4022	0·892	1·1	—	—	12·3
$BrCl_2$	11·40	9·70	143	20	*B*	7·70	78—90	1·4100	0·971	1·25	0·28	0·8	8·9
Br_2Cl	13·70	9·70	265	20	*B*	6·40	78—98	1·4230	—	0·67	0·73	0·7	14·6
Br_2Cl	13·70	19·40 (2 mol.)	7	70	*B*	12·55	78—100	1·4280	—	0·68	1·38	5·5[a]	11·25
Br_3	8·00	4·95	120	20	*A*	4·35	99—100	1·4400	1·270[b]	—	1·3	—	7·75[c]
Cl_2I	3·20	2·20	6	70	*C*	—	—	—	—	—	—	2·1[d] 96%	3·20[e]
Br_2I	16·45	8·75	6	70	*C*	0·20	100	—	—	—	—	7·45[f] 86%	15·50[g]
ClI_2	15·70	8·30	6	70	*C*	0·30	—	—	—	—	—	6·20[h] 75%	13·80[i]

(*a*) On distillation gave some dibutyl sulphate (2·3 g.), b. p. 56—74°/0·4 mm., n_D^{18} 1·4315, which can be obtained by the interaction of alkyl sulphite and alkyl chlorosulphonate (see Levaillant, *Compt. rend.*, 1933, **197**, 648). (*b*) Found: Br, 57·6. Calc. for C_4H_9Br: Br, 58·3%. (*c*) After recrystallisation from glacial acetic acid, pyridine hydrobromide (3·75 g., 0·95 mol.), m. p. 210—213° (Found: Br, 49·6. Calc. for C_5H_6NBr: Br, 50·0%), was obtained. (*d*) Di-*n*-butyl sulphite, b. p. 104°/12 mm., n_D^{20} 1·4280. (*e*) M. p. 187° (Found: equiv. of available halogen/mole, 1·91). (*f*) Di-*n*-butyl sulphite, b. p. 102°/8 mm., n_D^{20} 1·4280. (*g*) M. p. 173° (Found: equiv. of available halogen/mole, 1·91). (*h*) Di-*n*-butyl sulphite, b. p. 110°/20 mm. (*i*) Found: equiv. of available halogen/mole, 1·97.

TABLE 3.

Alcohol	$(RO)_2SO$ (g.)	C_5H_5NHBr (g.) *	Alkyl bromide				
			Yield (%)	B. p.	n_D^{20}	Br (%) Found	Br (%) Calc.
Butan-2-ol	4·70	(i) 0·02	75	92°	1·4380	57·9	58·4
		(ii) 4·00	63	92	1·4380	58·2	
Allyl alcohol	3·70	(i) 0·05	61	70	1·4673	65·7	66·05
		(ii) 4·00	6	70	1·4620	—	—
But-1-en-3-ol	3·83[a]	(i) 0·03	74	98—102	1·4750	57·6	59·2
		(ii) 6·40	48	100—104	1·4740	58·1	
Hex-1-en-3-ol	4·92[b]	(i) 0·02	56	68—70/45 mm.	1·4680	47·6	49·0 †
		(ii) 6·40	21	70/50 mm.	1·4633	47·1	
2-Methylpent-2-en-4-ol	4·92[c]	(i) 0·02	40	80—90/10 mm.	1·4995	46·8	49·0 †
		(ii) 6·40	14	80—90/10 mm.	1·4993	—	
2-Methylpent-1-en-4-ol	4·92[d]	(i) 0·02	34	66—70/7 mm.	1·4990	44·6	49·0 †
		(ii) 6·40	21	66—70/7 mm.	1·4990	45·7	

* (i) 0·01 Mol.; (ii) 2 mol.

† Available material was too small for further purification to be practicable.

(*a*) B. p. 98°/20 mm., n_D^{20} 1·4463 (Found: S, 16·7. $C_8H_{14}O_3S$ requires S, 16·9%). (*b*) B. p. 98—100°/0·1 mm., n_D^{20} 1·4630 (Found: S, 13·3. $C_{12}H_{22}O_3S$ requires S, 13·0%). (*c*) B. p. 98°/1·0 mm., n_D^{20} 1·4561 (Found: S, 12·5. $C_{12}H_{22}O_3S$ requires S, 13·0%). (*d*) B. p. 90—93°/1·0 mm., n_D^{20} 1·4570 (Found: S, 12·8. $C_{12}H_{22}O_3S$ requires S, 13·0%).

In Table 3 are shown the marked differences in the yields of alkyl bromide formed when thionyl bromide is added to the sulphite of an unsaturated alcohol in the presence of either 0·01 mol. or 2 mols. of pyridine hydrobromide. The pyridinium tribromide present in quantity can be used up in brominating the double bond, whereas when only a small amount of tribromide is present, the main reactions correspond to (3) and (4) catalysed by the salt, either bromide or tribromide.

When correlating mechanisms with the rotatory power of the alkyl halide produced, it is essential to know the nature of every reaction contributing to the overall yield of that product. In Table 4 are recorded the yields and optical rotations of the specimens of

2-bromo-octane obtained under different conditions in the thionyl bromide system. It is clear that the highest yield and greatest retention of optical activity (inversion of configuration) occur when thionyl bromide is added to the sulphite in the presence of a *trace* of pyridine hydrobromide (see Frazer, Gerrard, Machell, and Shepherd, *Chem. and Ind.*, 1954, 931).

TABLE 4.

Reactants	ROH α_D^{20} (l = 1)	Yield (%) [a]	B. p./ mm.	n_D^{20}	d_4^{20}	Br (%) [b]	α_D^{20} (l = 1)	% Retention of optical activity (inversion) [c]
$(RO)_2SO + SOBr_2 + C_5H_6NBr$ (0·01 mol.)	−7·64°	71·3	72°/10	1·4495	1·093	40·6	+36·72°	87
$(RO)_2SO + SOBr_2$ alone [d]	−7·60	57·6	76/12	1·4500	—	41·4	+36·00	86
$2ROH + 2SOBr_2 + 2C_5H_5N$ (2 mol.)	−7·64	51·3	72/10	1·4500	1·093	41·9	+35·80	85
$(RO)_2SO + SOBr_2 + C_5H_6NBr$ (2 mol.) ...	−7·64	53·8	72/10	1·4492	—	41·05	+35·20	84
$2ROH + 2SOBr_2$	−7·64	50·6	72/10	1·4497	1·098	40·9	+34·32	82
$(RO)_2SO + C_5H_5NHBr_3$	−7·60	45·0	82/15	1·4505	1·101	41·2	+28·72	68·5
$(RO)_2SO + C_5H_5NHBr_3$ [e]	−6·62	45·0	74—76/11	1·4500	1·097	41·7	+23·12	64
$(RO)_2SO + Br_2$ [f]	−7·60	29·8	78/12	1·4522	—	41·9	+24·00	57

(*a*) The yields in all cases are based on an expectation of 2 mol. of the bromide. (*b*) Calc. for $C_8H_{17}Br$: Br, 41·4%. (*c*) Calculated on the assumption that the (−)-ROH (α_D^{20} −8·00°) gives the (+)-RBr (α_D^{20} +44·00°) (Gerrard, *J.*, 1945, 848). (*d*) At 60° for 3 hr. (*e*) At 20° for 192 hr. (*f*) At 70° for 1·5 hr.

EXPERIMENTAL

Formation of Pyridinium Polyhalides.—Although the polyhalides were made from the base hydrohalide and thionyl halide by Frazer and Gerrard (*loc. cit.*), for the present purpose some of these were prepared by the addition of halogen to the monohalide, and were recrystallised from glacial acetic acid. Details are shown in Table 1. Analyses were carried out as described by Frazer and Gerrard (*loc. cit.*). Thionyl bromide was prepared by their method (*Chem. and Ind.*, 1954, 280).

*Interaction of Pyridinium Polyhalides and Di-*n*-butyl Sulphite.*—The results are shown in Table 2. For polyhalides containing iodine the amount of dibutyl sulphite recovered is shown in the column headed " 2nd Fraction." In the other cases, sulphur dioxide was evolved, and the colour of the polyhalide faded.

The methods of isolating the alkyl halide were as follows : (*A*) The halide was removed from the reaction mixture at 20°/10 mm. (1 hr.) and collected at −80°. (*B*) The supernatant liquid was decanted off, and process (*A*) used to complete removal from residue. The liquids were combined. (*C*) The mixture was filtered and washed with anhydrous ether (50 c.c.), the ether removed from the filtrate, and the residue dried at 10 mm.

The composition of the reaction product (1-chloro- and 1-bromo-butane) was estimated from the refractive index of the mixture, a graph constructed from the refractive indices of mixtures of known composition being used.

Interaction of Thionyl Bromide and the Sulphites of a Number of Unsaturated Alcohols in the Presence of Pyridine Hydrobromide (i, 0·01 *Mol.*; ii, 2 *Mols.*).—The results are shown in Table 3. Thionyl chloride (0·5 mol.) in anhydrous ether (25 c.c.) was added slowly (0·25—0·5 hr.) to a mixture of pyridine (1 mol.) and the alcohol (1 mol.) in ether (25 c.c.) at −80°. The pyridine hydrochloride was filtered off, the ether removed at 10 mm., and the sulphite distilled. To the sulphite (1 mol.), at −80°, were added pyridine hydrobromide (i, 0·01 mol.; ii, 2 mols.) and thionyl bromide (1 mol.). The mixture was allowed to warm to 20° (10 min.) and then heated to 70° for 3 hr., whereupon there was a vigorous evolution of sulphur dioxide. The reaction mixture was added to water (10 c.c.) and the oily layer was separated and distilled. A higher-boiling fraction was also obtained, leaving a black solid residue.

Interaction of Thionyl Bromide (1 *Mol.*) *with Pyridine* (1 *Mol.*) *and Allyl Alcohol* (1 *Mol.*).—Thionyl bromide (20·80 g., 1 mol.) was added (0·75 hr.) to a mixture of allyl alcohol (5·80 g., 1 mol.) and pyridine (7·90 g., 1 mol.) at −10°. The mixture was heated at 100° for 3 hr., whereupon sulphur dioxide was evolved and the precipitate dissolved. On cooling, a yellow solid formed which was added to water (50 c.c.) and extracted with ether (50 c.c.). The ethereal solution was dried ($MgSO_4$) and distilled, giving a mixture of ether and allyl bromide, b. p. 39—45°, and then 1 : 2 : 3-tribromopropane (7·2 g., 0·25 mol.), b. p. 92°/8 mm., n_D^{20} 1·5710, d_4^{20} 2·259.

Bromine was added to the first fraction until it was slightly red, the ether was removed at 10 mm., and the residue gave 1 : 2 : 3-tribromopropane (9·8 g., corresponding to allyl bromide, 35%), b. p. 103°/15 mm., n_D^{20} 1·5713.

Interaction of Pyridinium Tribromide and Allyl Alcohol.—Allyl alcohol (2·9 g., 1 mol.) was added quickly to pyridinium tribromide (16·00 g., 1 mol.). The solid was immediately decolorised with evolution of heat. The reaction mixture was added to water (20 c.c.) and extracted with ether (20 c.c.). The ethereal solution was dried ($MgSO_4$) and after removal of ether gave 2 : 3-dibromopropan-1-ol (7·1 g., 66%), b. p. 100°/8 mm., n_D^{18} 1·5600, d_4^{20} 2·122 (Found : C, 17·0; H, 2·7. Calc. for $C_3H_6OBr_2$: C, 16·5; H, 2·8%). The aqueous washings contained 3·9 g. of bromine (Calc. for 1 mol. of C_5H_6NBr : 4·0 g.).

Formation of (+)-2-*Bromo-octane.*—The reactants shown in Table 4 were heated at 70° for 3 hr. and then the reaction mixture was dissolved in water (15 c.c.), extracted with ether (20 c.c.), dried ($MgSO_4$), and the ether removed. After initial distillation of the (+)-2-bromo-octane, traces of alcohol were removed by means of thionyl chloride and pyridine, before final distillation.

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