Interaction of Trialkyl Phosphates and Boron Tribromide

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Trialkyl phosphates react with boron tribromide to yield alkyl bromides and a residue which affords tetragonal boron phosphate on ignition above 520°. Alkyl halide formation is more rapid than with boron trichloride. The isomeric purity of the bromides first formed is in accord with intermediate complex formation rather than bromine–alkoxyl exchange, at least for the n-alkyl esters and for tri-1-methylheptyl phosphate in petroleum solvent. In the absence of solvent, s-alkyl esters (1-methylbutyl, 1-ethylpropyl, and 1-methylheptyl) give bromides with much rearrangement.

TRIALKYL PHOSPHATES have previously been shown to react with boron trichloride to form 1 : 1 complexes which are fairly stable at room temperature but which afford alkyl chloride when heated in stages from 120 to 300°.[1] With boron tribromide the formation of alkyl halide is much more rapid and makes direct evidence for complex formation difficult to obtain. The n-propyl system, for example, gave n-propyl bromide (0·34 mol.)

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[1] W. Gerrard and P. F. Griffey, *Chem. and Ind.*, 1959, 55; *J. Chem. Soc.*, 1960, 3170; 1961, 4095.

immediately, upon warming from −80 to 20°. At 100—140° most of the remaining alkyl bromide was evolved, with a few per cent of rearrangement of n- to s-alkyl groups, indicative of some carbonium ion formation at this temperature. The formation of isomerically pure n-alkyl bromides in the initial stages of reaction shows that bromine–alkoxyl exchange (cf. boron trihalide–trialkyl phosphite systems [2]) does not occur, since the alkyl dibromoborinates which would be thus formed are known to decompose to yield rearranged alkyl bromides.[3] The results are in accord with the intermediate formation of a complex $(RO)_3PO,BBr_3$ similar to that obtained with boron trichloride,[1] followed by direct elimination of alkyl bromide in an S_N2 process: $Br^- \longrightarrow [RO{\cdot}PO(OR)_2,BBr_2]^+$.

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(RO)$_3$PO taken		Addition	Further reaction [a]		RBr isolated [b]		
R	Wt. (g.)	temp.	Temp.	Time	Mol.	α_D^{25} (l = 1)	Composition (%)
Et	40·2	−80°	20°	12 hr.	1·19	—	Et, 100
			100	1	0·86	—	,, 100
			300	1	0·12	—	—
Pr^n	44·7	−80	20	0 [c]	0·34	—	Pr^n, 100
			100	1	2·05	—	,, 93; Pr^i, 7
Pr^i	8·7	20	20	0 [c]	1·09	—	Pr^i, 100
			100	1	1·13	—	,, 98; Pr^n, 2 [d]
			300	1	0·04	—	—
Bu^n	21·0	−80	25	3	0·89	—	Bu^n, 100
			100	1	1·19	—	,, 99; Bu^s, 1
			140	1	0·29	—	,, 95; ,, 5
			300	1	0·02	—	—
Bu^i	10·8	−40	15	4	0·16	—	Bu^i, 96; Bu^t, 4
			100	1	1·76	—	,, 51; ,, 49
			200	1	0·11	—	—
			300	1	0·01	—	—
Bu^s	11·9	0	20	1	1·80	—	Bu^s, 100
			100	1	0·46	—	,, 100
$Me[CH_2]_2{\cdot}CHMe$ (Pe^2)	11·1	20	20	0 [c]	0·66	—	Pe^2, 77; Pe^3, 23
			20	24	0·90	—	
			100	1	0·72	—	,, 70; ,, 30
			300	1	0·09	—	—
Et_2CH (Pe^3)	9·3	20	20	0 [c]	1·47	—	Pe^3, 42; Pe^2, 58
			100	1	0·40	—	,, 19; ,, 81
			300	1	0·22	—	—
$Me[CH_2]_5{\cdot}CHMe$ [e] (Oc^2)	5·2	20	20	240	0·82	+8·26°	Oc^2, 56; Oc^3, 26; Oc^4, 18
			80	2	1·11	+5·16	,, 52; ,, 30; ,, 18
			120	1	0·20	+2·00	,, 61; ,, 23; ,, 16
			300	1	0·12	—	,, 81; ,, 11; ,, 8
$Me[CH_2]_5{\cdot}CHMe$ [e] (Oc^2)	9·2	−80 [f]	20	240	0·70	+38·16	Oc^2, 100
			20	168	0·55	+38·54	,, 100
			90	1	0·20	+22·92	,, 89; Oc^3, 8; Oc^4, 3
			140	1	0·40	+6·70	,, 62; ,, 22; ,, 16
			300	1	0·05	—	,, 82; ,, 12; ,, 6

[a] Successive periods for the ester taken. [b] In most experiments the reactants lost weight equivalent to RBr (2·8—2·9 mol.). Discrepancies between this and the weight isolated were shown to be due to inefficient trapping of the high-temperature products. [c] RBr removed immediately at 20°. [d] By g.l.c. Too small for infrared confirmation. [e] α_D^{25} − 16·54° (l = 1), from octan-2-ol α_D^{20} − 7·55° (l = 1). [f] Both reactants in light petroleum (b. p. 30—40°) (12 ml.); removed under reduced pressure at 20°.

Reaction of boron tribromide with tri-s-alkyl phosphates was particularly rapid. Upon mixing at −80° and warming to room temperature, sudden and violent decomposition was liable to occur. In most cases, therefore, the reagents were mixed slowly at 20° and afforded alkyl bromides (more than 1 mol.) immediately. Much rearrangement to isomeric bromides was observed for the 1-methylbutyl, 1-ethylpropyl, and (−)-1-methylheptyl systems, and was accompanied in the third case with considerable loss in optical rotatory power. As 3-bromopentane did not isomerise after formation (it was recovered without rearrangement when added to the tri-n-butyl phosphate–boron tribromide reaction), carbonium ion intermediates were assumed to be formed. On this basis it was not possible to rule out the occurrence of halogen–alkoxyl exchange in the s-alkyl systems. The addition of boron tribromide to (−)-tri-1-methyl heptyl phosphate in light petroleum at −80°, however, followed by solvent removal under reduced pressure at 20°, yielded isomerically pure 2-bromo-octane with more than 90% inversion of configuration, showing that by this procedure at least, the s-alkyl bromide was not formed through the intermediacy of the dibromoborinate.

Polymer networks of –P–O–B–O– linkages are thought to build up in phosphate–boron trihalide reactions,

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[2] W. Gerrard and M. Lindsay, *Chem. and Ind.*, 1960, 152.

[3] W. Gerrard, H. R. Hudson, and W. S. Murphy, *J. Chem. Soc.*, 1964, 2314.

during the elimination of alkyl halide; ignition to 1000° affords boron phosphate.[1,4] The residues left after heating to 300° have now been examined by *X*-ray powder photography but showed no crystalline structure. After ignition to 520° or higher, however, the tetragonal boron phosphate structure was clearly present.

EXPERIMENTAL

Starting Materials.—Commercially available trialkyl phosphates (Et, Pr^n, Bu^n) were distilled before use. Other trialkyl phosphates were prepared by described methods from phosphorus oxychloride[5] (Pr^i, Bu^s, Bu^i) or phosphorus oxybromide[6] (1-methylbutyl, 1-ethylpropyl, 1-methylheptyl), and alcohols which had been redistilled and checked for isomeric purity by g.l.c. Boron tribromide was obtained from the American Potash and Chemical Corporation.

Procedure.—Boron tribromide (1 mol.) was added dropwise to the phosphates under the specified conditions (Table). After the stated periods of time, alkyl bromides were removed under reduced pressure, trapped at −80°, washed, dried (K_2CO_3), distilled, and analysed as previously described for these halides (Br content, g.l.c., and infrared analysis).[7]

Reaction in the Presence of 3-Bromopentane.—Boron tribromide (9·2 g., 1 mol.) was added dropwise to tri-n-butyl phosphate (9·7 g., 1 mol.) and 3-bromopentane (3·8 g., 1 mol.) at −40°. After warming to 20° and allowing to stand (20 hr.), n-butyl bromide containing isomerically pure 3-bromopentane was removed under reduced pressure.

Examination of the Residues.—Polymeric residues, obtained on ignition of trialkyl phosphate–boron tribromide reaction products to the specified temperatures (below), were ground, screened to afford particles of <300 mesh, and examined with a 9-cm. Unicam *X*-ray powder camera using Cu K_α radiation. n-Propyl and s-butyl residues (both 300°) showed no diffraction pattern. 1-Methylheptyl (520°), n-propyl (600°), and s-butyl (1000°) residues gave patterns identical with that for tetragonal BPO_4 in the Powder Diffraction File of the American Society for Testing and Materials, but with a few weak extra lines corresponding to interplanar distances *d* (Å) 3·40, 1·69, 1·42, 1·40, 1·13, 1·10. These extra lines were also recorded for boron phosphate prepared by the ignition to 1000° (6 hr.) of ammonium dihydrogen phosphate with boric oxide.

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[4] W. Gerrard, *J. Oil Colour Chemists' Assoc.*, 1959, **42**, 625.
[5] W. Gerrard, *J. Chem. Soc.*, 1940, 1464.
[6] J. Fertig and W. Gerrard, *Chem. and Ind.*, 1956, 1457.
[7] W. Gerrard and H. R. Hudson, *J. Chem. Soc.*, 1963, 1059; 1964, 2310.