796. *Interaction of Boron Chlorides with Dialkyl or Diaryl Hydrogen Phosphites.*

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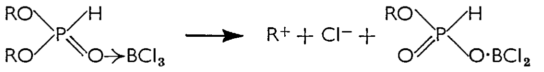
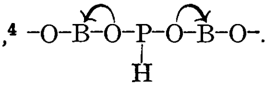
Dialkyl hydrogen phosphites form 1 : 1 complexes, $(RO)_2PH(:O),BCl_3$, which extrude alkyl chloride by a carbonium-ion mechanism. Hydrogen chloride is also formed, and the resulting network of O–P–O–B– links is ultimately found as boron phosphate. Diphenyl hydrogen phosphite and boron trichloride gave hydrogen chloride and primarily dichloroboron diphenyl phosphite, $(PhO)_2P\cdot O\cdot BCl_2$, which reacted further in accordance with the low electrophilic function of phenyl. Alkyl halide is eliminated on interaction of phenylboron chlorides and dialkyl hydrogen phosphites.

Trialkyl phosphites and boron trichloride readily exchange alkoxyl and chlorine when the alkyl group is of ordinary reactivity, as with n-butyl;[1] triphenyl phosphite reacted similarly,[2] there being no evidence of prior formation of a complex. Trialkyl phosphates, however, do form complexes, $(RO)_3P(:O),BCl_3$, which on being heated extrude alkyl chloride and form compounds with a network of O–P–O–B– linkages.[3] Similar complexes from triaryl phosphates are thermally stable.[2] It was therefore pertinent to examine the hydrogen phosphite esters.

Dialkyl hydrogen phosphite, $(RO)_2PHO$ ($R = Et, Pr^n, Pr^i, Bu^n, Bu^i$, or 1-methylheptyl), immediately formed the complex, $(RO)_2PH(:O),BCl_3$, which as shown by infrared spectra entails co-ordination between boron and the double-bonded atom of oxygen. When $R = Et, Pr^n$, or Bu^n, the complex gave alkyl chloride very slowly at 20°, but when heated in stages to 300°, evolves alkyl chloride (~2 mol.), mainly (1·5 mol.) at 50—80°. Hydrogen chloride was evolved more slowly, and even at 300° the solid residue contained easily hydrolysed chlorine.

The isopropyl complex decomposed steadily at 20°, giving isopropyl chloride (1·07 mol. in 0·5 hr.); otherwise the results were similar; and not only was the isobutyl rather less stable than the n-butyl complex, but the alkyl chloride evolved comprised a mixture of isobutyl (~30%) and t-butyl (~70%) chloride. Further, the complex from the (+)-1-methylheptyl ester gave the racemised alkyl chloride (2 mol.) in 70 hr. at 20°; and the rate of decomposition of the n-propyl complex at 20° was considerably increased by ferric chloride. These results point to the extrusion of alkyl chloride by a carbonium-cation mechanism. The first stage of the reaction may be depicted as follows:



It is believed that hydrogen is eliminated as hydrogen chloride when the electron density on a phosphorus atom has been sufficiently reduced by attachment to two boron-oxy-groups, which will involve strong back co-ordination from oxygen to boron,[4]  $-O-B-O-\underset{\overset{|}{H}}{P}-O-B-O-$. When each residue is heated to 900° in an open crucible boron phosphate, $[PBO_4]_x$, is produced, containing substantially all the phosphorus and boron.

Diphenyl hydrogen phosphite gave no apparent complex; but at 20° it gave hydrogen chloride (0·93 mol.) and the compound $(PhO)_2P\cdot O\cdot BCl_2$, as indicated by infrared spectrum which showed the presence of P–O–B and BCl_2 groupings. This result could be due to

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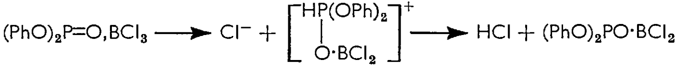
[1] Gerrard and Lindsay, *Chem. and Ind.*, 1960, 152.
[2] Frazer, Gerrard, and Patel, *Chem. and Ind.*, 1959, 90, 728; *J.*, 1960, 726.
[3] Gerrard and Griffey, *Chem. and Ind.*, 1959, 55.
[4] Abel, Gerrard, Lappert, and Shafferman, *J.*, 1958, 2895.

the preferential replacement on hydrogen because of the low electrophilic function of phenyl, or to a 4-centre broadside reaction between boron trichloride and the enolic form of the hydrogen phosphite.



$$(PhO)_2P{=}O,BCl_3 \longrightarrow Cl^- + \left[\begin{matrix}HP(OPh)_2\\ |\\ O{\cdot}BCl_2\end{matrix}\right]^+ \longrightarrow HCl + (PhO)_2PO{\cdot}BCl_2$$

Phenylboron dichloride reacted with diethyl hydrogen phosphite at 20°, giving ethyl chloride (1·9 mol.) during 48 hr. The residual infusible solid was soluble in methylene chloride, precipitated by pentane, and from analysis and infrared spectrum appeared to be $(PhBO_3PH)_n$, with the P–H bond intact. Phenylboronic acid was obtained by hydrolysis with hot water.

Diphenylboron chloride and di-n-butyl hydrogen phosphite gave n-butyl chloride (0·97 mol.) at 20° (17 days), but the white crystals, m. p. 126°, which were soluble in methylene dichloride (precipitated by pentane), although analysed, were not further characterised, the main point in these exploratory experiments being to show the formation of alkyl chloride.

EXPERIMENTAL

Dialkyl Hydrogen Phosphites and Boron Trichloride.—General procedure. The hydrogen phosphite (1 mol.) and boron trichloride (1 mol.) were mixed at −80°. Easily hydrolysed chlorine (e.h. Cl) and weight stability at 20°/20 mm. indicated 1 : 1 complex formation. This primary product was heated at the stated temperature, volatile matter being trapped at −80°, and in an alkali trap (for HCl). Alkyl chloride and hydrogen chloride were estimated by titration, analysis, and gas-chromatography. The weighed residue, which still contained easily hydrolysed chlorine, was heated at a higher temperature, volatile matter being again dealt with as stated. Finally, the residue was heated in an open crucible to about 900°, to obtain crystalline boron phosphate, the analysis of which usually conformed well with the calculated values (P, 29·3; B, 10·2%). Up to about 300°, essentially all the phosphorus and boron were in the residue; but at the higher temperatures there was some loss, especially of phosphorus, which appeared as phosphine and the element.

Results.—These are recorded in the table.

R in $(RO)_2PHO$	Temp.	Time (hr.)	RCl (mol.)	HCl (mol.)	R in $(RO)_2PHO$	Temp.	Time (hr.)	RCl (mol.)	HCl (mol.)
Et	100°	2	1·93	0·40	Bu^n	80°	0·5	1·80 [i]	0·28
	250	2	—	0·06		180	1		
Pr^n	80	1·75	1·23 [a]	—		300	6	0·06	0·3
	200	1	0·63	Trace	Bu^i	120	0·33	1·1 [j]	0·2
	300	5	0·09	0·18		230	2	0·9 [k]	0·4
Pr^n [b]	20	3	1·6 [c, d]	0·56 [d, e]					
Pr^i	20	0·08	1·07 [g]	0·07					
	20	30	0·16						
	300	2	0·54	0·41 [h]					

[a] B. p. 46° (Found: Cl, 45·8. Calc. for C_3H_7Cl: Cl, 45·2%). [b] In presence of ferric chloride (2% by wt.). [c] B. p. 46° (Found: Cl, 45·2%). [d] Both withdrawn at 20°/20 mm. [e] Residue (Found: e.h. Cl, 18·7%). [f] At 20°/18 mm. [g] B. p. 34·5° (Found: Cl, 45·2%). [h] Residue (Found: e.h. Cl, 6·3%). [i] B. p. 76·8° (Found: Cl, 38·0. Calc. for C_4H_9Cl: Cl, 38·5%). [j] By gas chromatography, Bu^iCl (0·3 mol.), Bu^tCl (0·8 mol.). [k] Similarly, Bu^iCl (0·3 mol.), Bu^tCl (0·6 mol.).

(+)-Di-(1-methylheptyl) Ester.—The ester (5·09 g.; α_D^{20} +12·24°) gave a complex which lost chlorine as alkyl chloride at 20° at such a rate that the easily hydrolysed chlorine content fell from 25·2% to 8·5% in 70 hr., and this corresponds to the formation of 2 mol. of alkyl chloride, which was extracted with methylene chloride (Found: Cl, 23·2. Calc. for $C_8H_{17}Cl$: Cl, 23·9%); it had α_D^{18} +0·10°.

When the complex was heated in stages to 250°, hydrogen chloride (0·95 mol.) was evolved, and eventually boron phophate (0·365 g. from 0·395 g. of residue) (Found: P, 29·1; B, 10·5%) was obtained.

Diethyl Hydrogen Phosphite and Phenylboron Dichloride.—The ester (10·9 g., 1 mol.) and the dichloride (12·5 g., 1 mol.) were mixed at 0°. Ethyl chloride (6·2 g., 1·2 mol.) was steadily evolved at 20° (72 hr.), and at 20°/20 mm. (2·7 g., 0·53 mol.) (2 hr.), leaving a white solid (14·5 g.) which contained entrapped ethyl chloride bringing the total yield to 9·87 g., 1·9 mol.

The white residue did not melt up to 300°. This *substance* was soluble in methylene chloride, from which it was precipitated by pentane (Found: P, 18·1; B, 6·4. $C_6H_6O_3PB$ requires P, 18·5; B, 6·5%). The infrared spectrum showed retention of the phosphorus–hydrogen bond. Hydrolysis afforded phenylboronic acid (90%), m. p. 216—218° (Found: B, 8·6. Calc. for $C_6H_7O_2B$: B, 8·9%).

Di-n-butyl Hydrogen Phosphite and Diphenylboron Chloride.—The ester (8·65 g., 1 mol.) was added to the chloride (8·95 g., 1 mol.) at 0°. At 20° n-butyl chloride (4·0 g., 0·97 mol.) was formed during 17 days, and then removed at 20°/20 mm. (Found: Cl, 38·2%). The residue (13·6 g.) was soluble in methylene dichloride and was precipitated therefrom by pentane. The solid, m. p. 126° (Found: C, 64·2; H, 6·4; P, 9·6; B, 3·34%; *M*, 312·4), was not examined further.

Diphenyl Hydrogen Phosphite and Boron Trichloride.—The ester (10·0 g., 1 mol.) and boron trichloride (7·1 g., 1·4 mol.) were mixed at −35°. As the system warmed to 0°, there was a copious evolution of hydrogen chloride (alkali trap became hot), but there was no vapour condensable at −80°. At 20° boron trichloride (2·0 g., 0·4 mol.) and hydrogen chloride (total, 1·45 g., 0·93 mol) were evolved. Of the yellow liquid residue (13·8 g.) (Found: Cl, 23·0; P, 9·6; B, 3·3. Calc. for $C_{12}H_{10}BCl_2O_3P$: Cl, 22·5; P, 9·8; B, 3·4%), 13·0 g. were heated at 0·5—0·1 mm. to afford phenyl phosphorodichloridite (2·55 g.) (trapped at −80°) (Found: Cl, 35·7; P, 15·4. Calc. for $C_6H_5Cl_2OP$: Cl, 36·4; P, 15·9%), and triphenyl borate (4·7 g.), b. p. 155°/0·05 mm., m. p. 89° (Found: B, 3·6. Calc. for $C_{18}H_{15}BO_3$: B, 3·7%). From the solid residue (2·75 g.) triphenyl borate (1·6 g.) was extracted by pentane, to leave a yellow solid (1·2 g.) which did not melt below 300° (Found: Cl, 0; P, 20·5; B, 10·0%). The alkali trap attached to the distillation apparatus contained chloride ion (1·17 g.) and phosphorus (0·33 g.) corresponding to 1·5 g. of phosphorus trichloride, and only a trace of boron.

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