800. *Interaction of Trialkyl Phosphates with Boron Trichloride.*

By W. Gerrard and P. F. Griffey.

Further facts on the formation and pyrolysis of trialkyl phosphate–boron trichloride 1 : 1 complexes relate to the formation of (—)-2-chloro-octane from the (+)-1-methylheptyl system, and the stability of the complex at 20°, when R = CH_2Bu^t, $Cl{\cdot}CH_2{\cdot}CH_2$, or $Cl_3C{\cdot}CH_2$. At elevated temperatures, the first gave t-pentyl chloride, and the second gave 1,2-dichloroethane and a residue having P–O–B grouping, whereas the third gave a mainly volatile products formed by exchange of alkoxyl and chlorine. Boron trichloride in excess of 1 mol. failed to give a higher complex with n-butyl phosphate; with the s-butyl system, hydrocarbon products (in benzene, s-butylbenzene) were produced.

Stepwise elimination of alkyl chloride from the complex of alkyl phosphate and boron trichloride, $(RO)_3PO,BCl_3$, (R = Me, Et, Pr^n, Pr^i, Bu^n, Bu^s, Bu^i, or n-pentyl), is confused by solidification of the system owing to the formation of polyanhydride, P–O–B, links.[1]

---

[1] Gerrard and Griffey, *Chem. and Ind.*, 1959, 55; *J.*, 1960, 3170.

The fact that the elimination of approximately one mol. of alkyl chloride (presumably mainly one alkyl group from each atom of phosphorus) is by an S_N2 (end-on) approach of a chlorine anion, is evident from the inversion without loss in optical purity in the 1-methylheptyl system and in the stability of the complex when R = neopentyl, $Cl{\cdot}CH_2{\cdot}CH_2$, or $Cl_3C{\cdot}CH_2$. Further elimination (under more forcing conditions) is by a carbonium-ion mechanism, in view of the optical result, the formation of t-pentyl chloride when R = neopentyl, and the formation of olefin and hydrogen chloride.

Thus (Table 1) at 20°, during 7 days, 2-chloro-octane (0·95 mol.) was formed with inversion and very little loss in optical activity, although on further removal of alkyl chloride (0·6 mol.) at 20°, and especially at 120° (0·33 mol.), there was a decided loss in rotatory power. At 120°, oct-2-ene and hydrogen chloride were also formed.

In conformity, the trineopentyl phosphate–boron trichloride complex (m. p. 91°) was stable for 1 month at room temperature, but gave t-pentyl chloride, hydrogen chloride, 2-methylbut-2-ene, and isopentane at 120° and 180°; isobutane instead of isopentane was obtained at 300°.

Tri-(2-chloroethyl) phosphate gave a liquid complex which was stable at 20°, but gave 1,2-dichloroethane (total yield, 2·60 mols.) on being heated (120°, 180°, 300°), hydrogen chloride (0·28 mol.) (300°) being the other identified volatile product. In contrast, the tri-(2,2,2-trichloroethyl) phosphate complex was stable at 120° for 1 hr., but at 150—160° reacted by the mutual exchange of alkoxyl and chlorine giving phosphoryl chloride, trichloroethyl phosphorodichloridate, tri-(2,2,2-trichloroethyl) borate, and the original phosphate, and only a comparatively small amount of non-volatile residue.

$$(Cl_3C{\cdot}CH_2{\cdot}O)_3PO,BCl_3 \longrightarrow POCl_3 + RO{\cdot}POCl_2 + (RO)_3B + (RO)_3PO$$

Boron trichloride did not react with tri-n-butyl phosphate in more than the 1 : 1 ratio.

However, the s-butyl 1 : 1 complex in methylene dichloride gave, with boron trichloride, a hydrocarbon product which appeared to comprise polymers of several s-butyl units; and when benzene was the solvent, s-butylbenzene was formed.

EXPERIMENTAL

Products were characterised by infrared-spectroscopic, gas-chromatographic, and chemical analyses. The general procedures for the preparation and pyrolysis of the 1 : 1 complexes have been described.[1] Easily hydrolysed chlorine is designated e.h.Cl, and was determined by treatment with water.

Boron Trihalide and Tri-[(+)-1-*methylheptyl*] *Phosphate.*—The phosphate, b. p. 154°/0·05 mm. (Found: P, 7·1. Calc. for $C_{24}H_{51}O_4P$: P, 7·1%) was prepared from (+)-octan-2-ol and phosphorus oxybromide in the presence of pyridine. Boron trichloride (3·16 g., 1 mol.) and the phosphate [11·67 g., 1 mol., α_D^{21} +17·15° (l = 1 dm.), from alcohol having α_D^{21} +6·76°, (l = 1 dm.)], when mixed in n-pentane (50 c.c.) at −76° and evaporated at 20°/20 mm., gave the liquid 1 : 1 *complex* (14·83 g.) (Found: e.h.Cl, 19·3. $C_{24}H_{51}BCl_3O_4P$ requires e.h.Cl, 19·3%). The complex was then decomposed as stated in Table 1, the 2-chloro-octane being removed at 0·1 mm. at the end of each period and characterised by distillation and gas chromatography. The reaction mixture became very viscous, and eventually solid. After final removal of volatile matter at 120°/0·1 mm., the solid residue contained 0·51 atom-equiv. of e.h. chlorine (corrected for removal of samples for analysis). The alkyl chloride obtained at 120° was mixed with oct-2-ene approximately equivalent in amount to the hydrogen chloride formed.

TABLE 1.

	Yield of RCl (mol.)	α_D^{23}	n_D^{20}	Yield of HCl (mol.)
7 days at 20°	0·95	−21·24°	1·4256	—
14 days at 20°	0·60	−18·44	1·4261	—
1 hr. at 120°	0·33	−11·64	1·4261	0·47

When (−)-2-chloro-octane, α_D^{21} −28·44°, was heated for 1 hr. at 120° with the powdered residue from pyrolysis of the n-butyl phosphate–boron trichloride complex at 120°, there was no loss in rotatory power.

Boron Trichloride and Trineopentyl Phosphate.—From the phosphate (14·27 g.) [b. p. 100°/0·5 mm., m. p. 93° (Found: P, 10·2. Calc. for $C_{15}H_{33}O_4P$: P, 10·0%)], the white solid 1 : 1 *complex* (19·69 g.) (Found: e.h.Cl, 24·2. $C_{15}H_{33}BCl_3O_4P$ requires e.h.Cl, 25·0%), m. p. 91°, was obtained, methylene dichloride (50 ml.) being the solvent. The complex was stored for a month without any loss in e.h. chlorine. After it (18·18 g.) had been heated at 120° for 10 min., a mixture (1·28 g.) of t-pentyl chloride (0·20 mol.) (correct infrared spectrum) and olefin was removed at 20 mm. and trapped at −80°. After 1 hr. the yield of t-pentyl chloride was 0·62 mol., and of hydrogen chloride 0·03 mol. Further amounts of these chlorides were obtained as follows: at 180° (1 hr.), $C_5H_{11}Cl$ (0·92 mol.), HCl (0·30 mol.); at 300° (1 hr.), $C_5H_{11}Cl$ (0·17 mol.), HCl (0·39 mol.); the final residue at 1000° was boron phosphate (4·34 g., corrected to undisturbed system. Calc. 4·52 g.). The products at 120° and 180° contained isopentane and 2-methylbut-2-ene, whereas at 300° isobutane was obtained instead of isopentane (infrared spectra and gas chromatography).

Tri-(2-chloroethyl) Phosphate–Boron Trichloride System.—The phosphate (16·12 g.) gave the liquid complex (22·73 g.), which afforded the following volatile products: at 120°, 1,2-dichloroethane (RCl, 1·18 mol.); at 180° (1 hr.), RCl (0·89 mol.); at 300° (1 hr.), RCl (0·53 mol.) and HCl (0·28 mol.). The final residue gave boron phosphate (5·77 g., corrected for undisturbed system. Calc., 5·97 g.). After the complex had been stored at 20° for 4 days, treatment with water afforded tri-(2-chloroethyl) phosphate in 92% yield.

Tri-(2,2,2-trichloroethyl) Phosphate–Boron Trichloride.—The phosphate (28·31 g.) gave the white solid *complex* (34·92 g.), m. p. 105° (Found: e.h.Cl, 17·2. $C_6H_6BCl_{12}O_4P$ requires e.h.Cl, 17·45%), which was stable at 120° (1 hr.). The complex (49·97 g.) was heated at 150—160° for 4 hr. Distillation then afforded fractions: (1) (1·86 g.), b. p. 26—61°/0·14 mm.; (2) (10·11 g.), b. p. 63—66°/0·12 mm.; (3) (7·51 g.), b. p. 84—106°/0·1—0·05 mm.; (4) (11·05 g.), b. p. 112—115°/0·05 mm.; (5) (7·69 g.), b. p. 159—164°/0·5 mm.; (6) (4·68 g.), trap (−80°) condensate; and (7) (2·07 g.), a solid residue. Infrared spectra and chemical analysis indicated products of mutual replacement of alkoxyl and halogen, which would require protracted fractionations for effective purification. The fractions were mainly: (2) trichloroethyl phosphorodichloridate (Found: P, 10·35. Calc. for $C_2H_2Cl_5O_2P$: P, 11·6%); (4) tri-(2,2,2-trichloroethyl) borate (Found: B, 1·8%); (5) the original phosphate. The trap condensate was phosphoryl chloride.

Interaction of Pyridine and the n-Butyl Complex.—The n-butyl phosphate–boron trichloride complex[1] (Found: e.h.Cl, 27·7. Calc. for $C_{12}H_{27}BCl_3O_4P$: Cl, 27·7%) (5·87 g., 1 mol.) was added to pyridine (1·25 g., 1 mol.) in n-pentane (50 c.c.) at 0°. After 24 hr., the pyridine–boron trichloride complex (2·21 g., 73·4%) was filtered off (Found: e.h.Cl, 54·7. Calc. for $C_5H_5BCl_3N$: e.h.Cl, 54·2%), and the filtrate afforded tri-n-butyl phosphate (3·26 g., 80%), b. p. 118°/0·7 mm. (Found: P, 11·7. Calc. for $C_{12}H_{27}O_4P$: P, 11·6%).

Influence of Boron Trichloride added in Excess of 1 *Mol.*—When n-butyl phosphate (25·94 g., 1 mol.) had been added to boron trichloride (22·91 g., 2 mol.) in methylene dichloride (50 c.c.) at −80° and the mixture stored at 0° for 7 days, boron trichloride (about 1 mol.) removed at 30 mm. was isolated as pyridine–boron trichloride complex (17·6 g., 0·92 mol.), m. p. 114—115°. The liquid residue (28·00 g.) (Found: e.h.Cl, 22·5%) corresponded empirically to the compound $(RO)_2PO{\cdot}O{\cdot}BCl_2$ (28·34 g.) (e.h.Cl, 24·4%), and was shown by its infrared spectrum to be essentially identical with a sample of n-butyl phosphate complex[1] which had lost about a third of its e.h. chlorine at room temperature. With water, the residue gave a clear solution and no oil.

To the s-butyl phosphate–boron trichloride complex[1] (13·2 g., 1 mol.) in methylene chloride (50 c.c.) at −80°, boron trichloride (3·83 g., 0·95 mol.) was added. At 0° a gel was quickly formed, and a solid separated from a liquid during 15 days. Volatile matter was removed at 20°/30 mm.; it contained boron trichloride (0·23 mol.) (isolated as the pyridine complex) and s-butyl chloride (2·6 g., 0·82 mol.). The residue was a pale yellow solid (9·61 g.) (Found: B, 5·9; e.h.Cl, 19·2; P, 11·2%), of which 6·78 g., with water, gave an oily hydrocarbon (1·33 g.) shown by distillation (b. p. 57—66°/0·2 mm., 115—123°/0·1 mm.) and by infrared study to be a mixture of several compounds, probably polymers of s-butyl units.

To the same s-butyl complex (16·22 g., 1 mol.) in benzene (20 c.c.), boron trichloride (4·82 g., 0·97 mol.) was added at −20°. At 0° a gel was quickly formed, and after 7 days volatile matter was removed at 20°/20 mm., finally at 20°/0·1 mm., and contained s-butylbenzene (0·9 g.) and a trace of s-butyl chloride. Of the bright yellow powder (19·48 g.) (Found: B, 3·6; e.h.Cl, 11·4; P, 6·7%), a portion (6·63 g.) was treated with water and the oil extracted with ether. The oil (3·38 g.) consisted mainly of s-butylbenzene, b. p. 170—172°, n_D^{20} 1·4898, and a mixture, probably of *m*- and *p*-di-s-butylbenzene (b. p. 115—118°/16 mm.), characterisation being based on infrared and gas-chromatographic examination.

The Northern Polytechnic, Holloway Road,
London, N.7.

[*Received, May* 3*rd*, **1961**.]