434. *Factors in the Formation of Isomerically and Optically Pure Alkyl Halides. Part IV.*[1] *The Three Dealkylation Steps in Phosphorus Trihalide* (Cl, Br, I)–*Alcohol Systems*

By E. J. Coulson, W. Gerrard, and H. R. Hudson

Previous evidence indicated two main sequences for the interaction of phosphorus trihalides, PX_3 (X = Cl, Br, or I), with alcohols of ordinary reactivity such as n-butanol and octan-2-ol, *viz.* the stepwise formation of trialkyl phosphite, and the stepwise dealkylation by hydrogen halide to form alkyl halide. We now present evidence to show that the first two dealkylations, for X = Cl or Br, give isomerically and optically pure (if ROH were optically pure) straight-chain alkyl halides, whereas the third leads to some rearrangement in 2- or 3-pentyl or 2-octyl, but not in n-alkyl, isopropyl, t-butyl, and (apparently) s-butyl groups. There is some loss in optical purity for the 2-octyl system in the third step. Similar results are obtained when X = I, except that 2-octyl iodide loses some optical purity in all three steps. For the isobutyl system (X = Cl or Br) some rearrangement occurs in each step, but not when X = I; for then, t-butyl iodide ($<1\%$) is isolated only from the third step.

Interaction of (+)-di-2-octyl hydrogen phosphite and phosphorus triiodide in carbon disulphide (no HI present) gives optically pure 2-octyl iodide.

With alcohols of ordinary reactivity, typified by n-butanol, formation of alkyl chloride in the phosphorus trichloride–alcohol systems appears to be mainly, if not entirely, by a series of stepwise reactions (1).[2]

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[1] Part III, W. Gerrard, H. R. Hudson, and W. S. Murphy, *J.*, 1964, 2314.

[2] W. Gerrard, *J.*, 1940, 1464; 1944, 85; W. Gerrard and E. G. G. Whitbread, *J.*, 1952, 914; W. Gerrard, M. J. D. Isaacs, G. Machell, K. B. Smith, and P. L. Wyvill, *J.*, 1953, 1920, and Papers cited therein.

$$\mathrm{3ROH + PCl_3 \xrightarrow{Quick} [ROPCl_2,(RO)_2PCl] \xrightarrow{Quick} (RO)_3P + 3HCl \xrightarrow{Quick} \underset{\text{1st dealkylation}}{RCl + (RO)_2P(O)H}}$$

$$\mathrm{\xrightarrow{slow} \underset{\text{2nd dealkylation}}{RCl + ROP(O)HOH} \xrightarrow{very\ slow} \underset{\text{3rd dealkylation}}{RCl + P(OH)_3}} \quad (1)$$

A similar series is discernible for the phosphorus tribromide system; but, presumably because the bromine anion is a stronger nucleophile, the dealkylations are correspondingly quicker, and other reactions can contribute alkyl bromide, usually to a small but significant extent, according to experimental conditions.[3] That the first and second dealkylations gave optically " pure " 2-chloro-octane, whereas the third involved considerable loss in optical purity,[4] led to the study of the phosphorus trihalide systems from the viewpoint of extent of rearrangement in the alkyl group during the formation of alkyl halide by each of the three dealkylations.

The alkyl groups ($\mathrm{Pr^n}$, $\mathrm{Bu^n}$, $\mathrm{Pe^n}$, $\mathrm{Oc^n}$, $\mathrm{Pr^i}$, and $\mathrm{Bu^s}$) gave isomerically pure halides (Cl, Br) by each of the three dealkylations. Halides from the first, very rapid, dealkylation were readily isolated by quenching the reactants in ice–water immediately after mixing at −10° or, in the case of bromides, by removal of excess of hydrogen bromide in a stream of nitrogen. s-Alcohols having alternative isomeric secondary structures ($\mathrm{Pe^2}$, $\mathrm{Pe^3}$, $\mathrm{Oc^2}$), previously stated to give rearranged halides in their reactions with phosphorus tribromide,[5] thus gave isomerically, and (presumably) optically, pure products. Octan-2-ol, α_D^{20} $+8{\cdot}02°$ ($l = 1$) * gave 2-chloro-octane α_D^{20} $-30{\cdot}76°$ ($l = 1$), and 2-bromo-octane α_D^{20} $-44{\cdot}91°$ ($l = 1$). As treatment of the dialkyl hydrogen phosphites so produced with <1 mol. of hydrogen chloride or bromide always yielded an isomerically pure s-halide (RCl, α_D^{20} $-30{\cdot}97°$; RBr, α_D^{20} $-44{\cdot}33°$) whilst treatment with >1 mol. led to some rearrangement and loss in rotatory power (Tables 4 and 5), it is concluded that rearrangement occurs only in the third dealkylation step. Rearrangement of the halide *after* formation did not occur, as (+)-2-chloro-octane was unaffected in 85 days under reaction conditions, and (−)-2-bromo-octane, although losing some rotatory power (8·9%) was not rearranged in 261 hours under similar conditions. The possibility of rearrangement of the alkyl group in the monoalkyl dihydrogen phosphite *before* dealkylation appears unlikely, although in any event it is from the final dealkylation that the rearranged halide is obtained.

Pure isobutyl halides (Cl, Br) were unobtainable in these phosphorus trihalide systems. The first dealkylations gave t-halides (*ca.* 1%), the second gave t-halides (*ca.* 3%), and the third gave t-butyl chloride (28%) or bromide (10%).

From t-butyl alcohol the t-butyl halide exclusively was quickly formed without revelation of the reaction sequence. It appears highly probable that after a small amount of hydrogen halide has been produced by the first step:

$$\mathrm{ROH + PX_3 \longrightarrow ROPX_2 + HX,}$$

the bulk of the t-butyl halide is formed by the cycle:

$$\mathrm{HX + Bu^tOH \longrightarrow Bu^tX + H_2O}$$

$$\mathrm{3H_2O + PX_3 \longrightarrow 3HX + P(OH)_3}$$

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* α_D^{20} $+8{\cdot}02°$ ($l = 1$) has been taken as the maximum for octan-2-ol, from Pickard and Kenyon's figures, $[\alpha]_D^{20}$ $+9{\cdot}76$; d_4^{20} 0·8214 (*J.*, 1911, 45). α_D^{20} $+8{\cdot}15°$ ($l = 1$), which was reported by Brauns (*Rec. Trav. chim.*, 1946, **65**, 803) and used in recent calculations by Hoffmann,[8] was based on measurement in a 0·2 dm tube and may be less accurate.

[3] W. Gerrard, *J.*, 1945, 848; W. Gerrard and H. Herbst, *J.*, 1955, 277; V. F. G. Cooke and W. Gerrard, *J.*, 1955, 1978, and Papers cited therein.

[4] T. M. Cook, E. J. Coulson, W. Gerrard, and H. R. Hudson, *Chem. and Ind.*, 1962, 1506.

[5] M. L. Sherrill, B. Otto, and L. W. Pickett, *J. Amer. Chem. Soc.*, 1929, **51**, 3023; M. L. Sherrill, C. Baldwin, and D. Haas, *ibid.*, p. 3034; H. Pines, A. Rudin, and V. N. Ipatieff, *ibid.*, 1952, **74**, 4063; J. Cason and J. S. Correia, *J. Org. Chem.*, 1961, **26**, 3645.

In the hydrogen iodide systems, no rearrangement occurred with the straight-chain n-alkyl groups, or with Pr^{i} or Bu^{s}; but did so with Pe^{2}, Pe^{3}, and Oc^{2} groups in the third step (Table 6). Again, rearrangement of the halide after formation was excluded, as (+)-2-iodo-octane was unrearranged under reaction conditions after 360 hours, although it lost some rotatory power (9·8%) in this time. Loss in optical purity of 2-iodo-octane isolated during the early stages of dealkylation, could have been due to S_N2 anionic (I^-) exchange after initial formation. In the isobutyl system, no rearrangement occurred in the second stage and <1% t-butyl iodide was isolated in the third. Phosphorus tri-iodide, solid or in carbon disulphide (Table 7), formed the alkyl halide more slowly than when X = Cl or Br. It is probable that optically pure 2-iodo-octane was formed in the early stages, but lost rotatory power on longer contact with the hydrogen iodide in solution.

Interaction of di-2-octyl hydrogen phosphite (from ROH, α_D^{20} +8·02°) with phosphorus tri-iodide in carbon disulphide (no hydrogen iodide present), gave 2-iodo-octane, α_D^{20} −64·63°, slightly higher than the previous highest recorded value.[6]

Contrary to a previous conclusion[7] that there is no satisfactory method for demonstrating the optical purity of alkyl halides when halogen is at the asymmetric centre, Hoffmann has recently described a procedure for so doing in the example of the 2-octyl halides.[8] The procedure did not entail the preparation of " optically pure " halides; but, by converting the " best value " halides into a thioether by a stereospecific reaction, the optical purity of the alkyl halides was estimated. Hoffmann's estimated maximum α_D^{20} values are RCl, 32·4°; RBr, 44·5°; RI, 64·2°, calculated for ROH, α_D^{20} +8·15°, and do not differ materially from those previously[2-4,6] and herein reported.

EXPERIMENTAL

Alcohols and alkyl halides were analysed by gas–liquid chromatography and infrared spectroscopy as described previously. Optical rotations are for l = 1 dm.

Reactions of Alcohols with Phosphorus Trihalides (Cl, Br).—The trihalide (0·33—0·38 mol.) was added dropwise with shaking (15—30 min.) to the alcohol (1 mol.) at −10°. To isolate the alkyl halide from the first dealkylation, the mixture was immediately added to ice–water, neutralised with potassium carbonate, and the organic layer (ether-extracted if necessary) was washed, dried (K_2CO_3), and distilled. Owing to the much more rapid further dealkylation of dialkyl phosphites by hydrogen bromide, it was necessary in some phosphorus tribromide systems to pass nitrogen rapidly through the mixture during addition to sweep away excess of the hydrogen bromide, and for 1 hr. more during warming to room temperature, before quenching (see Tables 1 and 2).

TABLE 1

Alcohol–phosphorus trichloride (0·33 mol.) reactions at −10°

ROH (1 mol.)		Alkyl halide (RCl)					Dialkyl phosphite $(RO)_2PHO$				
R	Wt. (g.)	Yield (mol.)	B. p./mm.	n_D^{20}	Composition (%)		Yield (mol.)	B. p./mm.	n_D^{20}	P (%)	
										Found	Calc.
Pr^{n}	93·7	0·34	46—50°	—	Pr^{n}	100	0·30	101—102°/17	1·4175	18·6	18·6
Pr^{i}	79·3	0·35	38	—	Pr^{i}	100	0·29	106—108/53	1·4089	18·5	,,
Bu^{n}	113·8	0·42	78	1·4018	Bu^{n}	100	0·23	84—86/0·6	1·4242	15·9	15·95
Bu^{s}	72·9	0·37	67—68	1·3960	Bu^{s}	100	0·27	82—84/0·7	1·4186	16·2	,,
Bu^{i}	46·5	0·25	68—69	—	Bu^{i}	>99[a]	0·32	108—109/7	1·4195	15·8	,,
Pe^{n}	68·9	0·27	107—108	1·4113	Pe^{n}	100	0·32	96—97/0·05	1·4287	14·0	13·9
Pe^{2}	55·1	0·26	95—97	1·4052	Pe^{2}	100	0·28[b]	73/0·1	1·4240	13·9	,,
Pe^{3}	142·3	0·27	97—98	1·4095	Pe^{3}	100	0·29	90—91/0·1	1·4277	13·9	,,
Oc^{n}	76·4	0·29	75/12	1·4295	Oc^{n}	100	0·29	151—153/0·03	1·4413	10·3	10·1
Oc^{2}	23·7[c]	0·31	35/0·6	1·4263	Oc^{2}	100[d]	0·23[e]	148—150/0·6	1·4370	10·2	,,

[a] Bu^{t}, <1%. [b] New compound, d_4^{20} 0·954. [c] α_D^{20} +7·98°. [d] α_D^{20} −30·60°; α_D^{20} −30·76° corrected for ROH, α_D^{20} +8·02°. [e] α_D^{20} +14·16°.

Pe^{n} = n-pentyl, Pe^{2} = Me·$[CH_2]_2$·CHMe, Pe^{3} = Et_2CH, Oc^{n} = n-Octyl, Oc^{2} = Me·$[CH_2]_5$·CHMe.

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[6] M. C. Berlak and W. Gerrard, *J.*, 1949, 2311.

[7] P. S. Skell, R. G. Allen, and G. K. Helmkamp, *J. Amer. Chem. Soc.*, 1960, **82**, 410.

[8] H. M. R. Hoffmann, *J.*, 1964, 1249. (His ref. No. 8 was omitted for RBr and RI in his Table.)

To isolate the alkyl halide from the complete sequence of reactions (*i.e.*, including the second and third dealkylation steps), the alcohol–phosphorus trihalide mixtures were stored in sealed tubes at 25° for the specified times (Table 3).

TABLE 2

Alcohol–phosphorus tribromide reactions at −10°

ROH (1 mol.)			Alkyl bromide (RBr)			
R	Wt. (g.)	PBr_3 (mol.)	Yield (mol.)	B. p./mm.	n_D^{20}	Composition (%)
Pr^n	9·6	0·33	0·31	71°	—	Pr^n 100
Pr^i	11·7	,,	0·15	58—59	1·4224	Pr^i 100
Bu^n	16·5	,,	0·29	99—100	—	Bu^n 100
Bu^s	14·3	,,	0·33	90—91	—	Bu^s 100
Bu^i	13·4	,,	0·27	88—90	1·4339	Bu^i 99·2; Bu^t 0·8
Pe^n	18·0	,,	0·35	124—129	—	Pe^n 100
Pe^2	17·0	,,	0·27	117—119	—	Pe^2 97·5; Pe^3 2·5
Pe^2	18·8	0·36 [a]	0·21	115	1·4370	Pe^2 100
Pe^3	24·0	0·33	0·26	116—118	—	Pe^3 100
Oc^n	24·1	,,	0·29	89—93/17	—	Oc^n 100
Oc^2	15·5 [b]	,,	0·21	89—91/22	1·4493	Oc^2 100 [c]
Oc^2	40·0 [d]	0·38 [a]	0·27	72/9	1·4491	Oc^2 100 [e]

[a] N_2 gas stream to remove HBr. [b] α_D^{20} +7·95°. [c] α_D^{20} −42·05°; α_D^{20} −42·41° corrected for ROH, α_D^{20} +8·02°. [d] α_D^{20} +7·42°. [e] α_D^{20} −40·24°; α_D^{20} −43·49° corrected. On a smaller scale with a rapid CO_2 stream, ROH, α_D^{15} +8·07°, gave RBr, α_D^{20} −44·0°; α_D^{20} −44·91° corrected (ref. 9).

TABLE 3

Alcohol–phosphorus tribromide (0·33 mol.) reactions at 25°

ROH (1 mol.)			Alkyl bromide (RBr)			
R	Wt. (g.)	Time (hr.)	Yield (mol.)	B. p./mm.	n_D^{20}	Composition (%)
Pr^n	6·9	125	0·72	69—70°	1·4335	Pr^n 100
Pr^i	10·1	21	0·82	57—59	1·4247	Pr^i 100
Bu^n	12·2	170	0·81	101—102	1·4390	Bu^n 100
,,	12·6	261	— [a]			
Bu^s	7·8	21	0·83	89—90	1·4364	Bu^s 100
Bu^i	9·6	19	0·46	91	1·4340	Bu^i 98·6; Bu^t 1·4 [b]
,,	9·9	790	0·69	90—91	1·4335	,, 96·9; ,, 3·1 [c]
Pe^n	10·9	168	0·86	127—128	1·4443	Pe^n 100
Oc^n	20·4	168	0·83	87—88/16	1·4517	Oc^n 100

[a] Not isolated. 2-Bromo-octane (2·2 g.), α_D^{19} −20·38°, added to reactants was recovered (1·9 g.), b. p. 76—78°/15 mm., α_D^{19} −18·57°, representing 8·9% racemisation without rearrangement. [b] Calc. for 2nd step only: Bu^i 97·3; Bu^t 2·7%. [c] Calc. for 3rd step only: Bu^i 90·2; Bu^t 9·8%.

Reactions of t-Butyl Alcohol with Phosphorus Trihalides.—Addition of the trichloride (60·7 g., 0·33 mol.) to t-butyl alcohol (98·1 g.) at 20°, followed by immediate removal of volatile matter under reduced pressure, left white, crystalline phosphorous acid (36·4 g., 0·33 mol.), m. p. 56—62° (Found: P, 35·6. Calc. for H_3PO_3: P, 37·8%) and afforded t-butyl chloride (112·8 g., 0·92 mol.), b. p. 50—51°, n_D^{20} 1·3840.

Phosphorus tribromide (18·7 g., 0·33 mol.) and t-butyl alcohol (15·4 g.) similarly yielded phosphorous acid (5·9 g., 0·35 mol.), m. p. 64—74° (Found: P, 35·9%) and t-butyl bromide (27·8 g., 0·98 mol.), b. p. 71—72°, n_D^{20} 1·4275.

Reactions of Dialkyl Hydrogen Phosphites with Hydrogen Halides.—The phosphites (Table 1) obtained were treated with anhydrous hydrogen halide at 20° until the desired concentrations were reached and stored in sealed tubes at 25° for the specified times (Tables 4 and 5). For chlorides, the tubes were cooled to −80°, opened under dilute aqueous ammonia (for esimation of remaining hydrogen chloride), and the organic layer was washed and dried (K_2CO_3). The bromide products were treated with a small amount of anhydrous potassium carbonate and distilled directly.

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[9] W. Gerrard and H. R. Hudson, *J.*, 1964, 2310.

The Iodide Systems.—The dialkyl phosphites were treated with dry hydrogen iodide at 0° until the desired increase in weight had occurred. After being stored at room temperature for the specified periods (Table 6), volatile products were removed at low pressure, and the residue was treated with more hydrogen iodide to effect further dealkylation. In Table 7 are recorded results of the interaction of the alcohol with phosphorus tri-iodide dissolved in carbon disulphide. Unless otherwise stated, mixing was done at −10°. After storage at 25° for the stated times, ice was added, and the alkyl iodide was isolated as usual.

TABLE 4

Dialkyl hydrogen phosphite–hydrogen chloride reactions at 25°

(RO)$_2$PHO (1 mol.)					Alkyl chloride (RCl)			
R	Wt. (g.)	HCl (mol.)	Time (days)	HCl used (mol.)	Yield (mol.)	B. p./mm.	n_D^{20}	Composition (%)
Pr^n	30·3	1·43	117	1·15	1·06	47°	1·3882	Pr^n 100
Pr^i	17·7	2·16	169	2·02	1·55	34—35	1·3779	Pr^i 100
Bu^n	12·6[a]	1·85	85	1·40	1·13	77—78	1·4016	Bu^n 100
Bu^s	22·4	1·47	47	1·43	1·42	68—69	1·3970	Bu^s 100
Bu^i	15·1	1·41	2	0·17	0·19	—	1·3976	Bu^i 96·8; Bu^t 3·2
,,	16·2	2·36	108	1·23	1·21	65—69	1·3956	,, 92·1; ,, 7·9[b]
Pe^n	24·7	1·53	55	1·45	1·38	108—109	1·4116	Pe^n 100
Pe^2	16·4	1·60	2	0·81	0·77	95	1·4051	Pe^2 100
,,	16·4	1·60	51	1·58	1·50	95—97	1·4050	Pe^2 91·8; Pe^3 8·2[c]
Pe^3	30·1	1·76	2	0·72	0·71	96—97	1·4086	Pe^3 100
,,	26·5	1·76	35	1·69	1·59	97	1·4080	Pe^3 97·8; Pe^2 1·2[d]
Oc^n	17·9	1·54	53	1·22	0·99	183—184	1·4341	Oc^n 100
Oc^2	15·7[e]	1·12	22	0·93	0·92	61—62/17	1·4257	Oc^2 100[f]
,,	6·2[g]	2·03	17	1·82	1·78	112—115/88	1·4260	Oc^2 96·8; Oc^3 2·7; Oc^4 0·5[h]

[a] 2-Chloro-octane (4·64 g.). α_D^{19} +29·87° added to reactants was recovered (2·87 g.), b. p. 94—95°/60 mm., n_D^{20} 1·4262, α_D^{20} +29·84°. [b] Calc. for 3rd step only: Bu^i 72; Bu^t 28%. [c] Calc. for 3rd step only: Pe^2 78; Pe^3 22%. [d] Calc. for 3rd step only: Pe^3 96·8; Pe^2 3·2%. [e] From ROH, α_D^{20} +5·78°. [f] α_D^{20} −22·32°; α_D^{20} −30·97° corrected for ROH, α_D^{20} +8·02°. [g] From ROH α_D^{20} −7·87°. [h] α_D^{20} +19·29°. Calc. for 3rd step only: Oc^2 93·2; Oc^3 5·7; Oc^4 1·1%; α_D^{20} +6·20° (α_D^{20} +6·78° for the Oc^2 only and corrected for ROH, α_D^{20} −8·02°, assuming the Oc^3 and Oc^4 to be inactive).

TABLE 5

Dialkyl hydrogen phosphite–hydrogen bromide reactions at 25°

(RO)$_2$PHO (1 mol.)				Alkyl bromide (RBr)			
R	Wt. (g.)	HBr (mol.)	Time (hr.)	Yield (mol.)	B. p./mm.	n_D^{20}	Composition (%)
Pe^2	9·6	0·57	2	0·52	116—118°	1·4390	Pe^2 100
,,	3·7	1·82	20	1·76	116—118	1·4372	Pe^2 85·6; Pe^3 14·4[a]
Pe^3	15·6	0·69	2	0·67	117—119	1·4412	Pe^3 100
,,	8·2	2·10	24	1·96	117—118	1·4434	Pe^3 82·7; Pe^2 17·3[b]
Oc^2	13·9[c]	0·68	2	0·59	73—74/0·6	—	Oc^2 100[d]
,,	5·0[e]	1·51	91	1·50	74—75/14	1·4496	Oc^2 91·7; Oc^3 7·7; Oc^4 0·6[f]

[a] Calc. for 3rd step only: Pe^2 67; Pe^3 33%. [b] Calc. for 3rd step only: Pe^3 65; Pe^2 35%. [c] From ROH α_D^{20} +3·68°. [d] α_D^{20} −20·34°; α_D^{20} −44·33° corrected for ROH, α_D^{20} +8·02°. [e] From ROH α_D^{20} +7·87°. [f] α_D^{20} −31·64°. Calc. for 3rd step only: Oc^2 75·1; Oc^3 23·1; Oc^4 1·8%; α_D^{20} −8·09° (α_D^{20} −10·98° for the Oc^2 only and corrected for ROH, α_D^{20} +8·02°, assuming the Oc^3 and Oc^4 to be inactive).

(−)-Di-2-octyl hydrogen phosphite (5·23 g.), α_D^{22} −8·94° (from ROH, α_D^{20} −4·58°) was added to a solution of phosphorus tri-iodide (7·05 g., 1 mol.) in carbon disulphide (60 ml.) at −10°. After 48 hr. at 20° ice was added. Distillation of the dried organic layer afforded (+)-2-iodo-octane (3·42 g., 0·83 mol.), b. p. 41°/0·5 mm., n_D^{20} 1·4879, α_D^{20} +36·91°. (Calc. α_D^{20} +64·63°, from ROH, α_D^{20} +8·02°) (Found: I, 53·2. Calc. for $C_8H_{17}I$: I, 52·9%). A solution of hydrogen iodide (0·24 g.) and 3-iodopentane (1·43 g.) in carbon disulphide (3·69 g.) was stored at 20° for 10 days. No isomerisation of the alkyl halide occurred.

TABLE 6

Dialkyl hydrogen phosphite–hydrogen iodide reactions at 25°

(RO)$_2$PHO (1 mol.)				Alkyl iodide	
R	Wt. (g.)	HI (mol.)	Time * (hr.)	Yield † (mol.)	Composition (%)
Pr^n	9·60 [a]	1·91	360	1·64	Pr^n 100
Bu^i	10·3	0·68	17	0·68	Bu^i 100; Bu^t 0
		0·93	70	0·53	,, 100; ,, 0
		0·87	168	0·34	,, *ca.* 100; Bu^t <1
Pe^2	10·3	0·40	24	0·37	Pe^2 100; Pe^3 0
		0·61	72	0·63	,, 97; ,, 3
		0·35	24	0·30	,, 83; ,, 17
		0·72	168	0·63	,, 74; ,, 26
Pe^3	10·1	0·45	24	0·45	,, trace; Pe^3 *ca.* 100
		0·53	72	0·53	,, 1; Pe^3 99
		0·69	24	0·72	,, 20; ,, 80
		0·43	48	0·17	,, 28; ,, 72
Oc^2	16·2	0·60	2·5	0·56	Oc^2 100
		0·89	14	0·73	,, 93; Oc^3 7; Oc^4 0
		0·64	72	0·52	,, 78; ,, 22; ,, trace
Oc^2	16·7 [b]	0·84	0·25	0·76 [c]	,, 100; ,, 0; ,, 0
		0·21	48	0·19 [d]	,, *ca.* 100; Oc^3 trace; Oc^4 0
		0·43	336	0·44 [e]	,, 89; Oc^3 11; Oc^4 0
Oc^2	3·4	2·2	480	1·51 [g]	,, 86; ,, 14; ,, 0

* Successive reaction periods for the phosphite named. † Obtained during that period.

[a] 2-Iodo-octane (2·02 g.), n_D^{20} 1·4879; α_D^{20} +36·91°, added. Recovered (1·0 g.) (Found: I, 53·0%), b. p. 37°/0·005 mm., n_D^{20} 1·4876, α_D^{20} +33·28°, without rearrangement. [b] α_D^{19} +14·32°, from ROH α_D^{20} +7·46°. [c] α_D^{20} −36·06°. α_D^{20} −38·77° corrected for ROH, α_D^{20} +8·02°. [d] α_D^{20} −36·10°. α_D^{20} −38·72° corrected for ROH, α_D^{20} +8·02°. [e] α_D^{20} −28·05°. α_D^{20} −33·89° calc. for the Oc^2 only and corrected for ROH, α_D^{20} +8·02°, assuming the Oc^3 and Oc^4 to be inactive. [f] α_D^{22} −8·94°, from ROH, α_D^{20} −4·58°. [g] α_D^{20} +27·27°. α_D^{20} +55·64° calc. for Oc^2 only and corrected for ROH, α_D^{20} −8·02°. Aqueous treatment before distillation.

TABLE 7

Alcohol–phosphorus tri-iodide reactions at 25°

ROH (1 mol.)				Alkyl iodide (RI)	
R	Wt. (g.)	PI$_3$ * (mol.)	Time (hr.)	Yield (mol.)	Composition (%)
Pr^i	2·22	0·33	504	0·28 [a]	Pr^i 100
Bu^n	2·74	0·33	504	0·77	Bu^n 100
Bu^s	2·74	0·33	504	0·44	Bu^s 100
Pe^2	6·68	0·33 [b]	1	0·16	Pe^2 100; Pe^3 0
,,	3·14	1·00	24	0·58	,, 93; ,, 7
Pe^3	3·14	1·00	24	0·65	,, 6; ,, 94
Oc^2	8·45 [c]	0·33	0·25	0·13 [d]	Oc^2 100
,,	5·00 [e]	1·00	24	0·63 [f]	,, 100
,,	5·00 [e]	1·00 [g]	24	0·29 [h]	,, 100

* Solution in CS$_2$ (216 g./l.).

[a] Low yield of Pr^{i}I has been noted previously (ref. 6). [b] ROH added to solid PI$_3$ at −80°; 1 hr. at 0°; product contained unreacted alcohol (0·16 mol.). [c] α_D^{20} +7·86°. [d] Obtained (b. p. 58°/0·5 mm.) mixed with unreacted alcohol; n_D^{20} 1·4593 indicates 68·5% w/w or 57% v/v RI. α_D^{20} −31·30°. α_D^{20} −62·1° calc. for RI only and corrected for ROH, α_D^{20} +8·02°. (This calculation was shown to be valid by use of synthetic mixtures.) Mixed di- and tri-2-octyl phosphites (3·70 g.), b. p. 148—150°/0·5 mm., n_D^{20} 1·4378, remained. [e] α_D^{20} −7·90°. [f] B. p. 30°/0·05 mm., n_D^{20} 1·4879, α_D^{20} +61·23°. α_D^{20} +62·17° corrected for ROH, α_D^{20} −8·02° (Found: I, 53·0%). [g] Plus pyridine (3·04 g., 1 mol.). Filtered before distillation, but no aqueous treatment. [h] First distillate (0·7 g.) (Found: I, 53·0%), b. p. 42°/0·5 mm., n_D^{20} 1·4872, α_D^{20} +61·70°. α_D^{20} +62·65° corrected for ROH, α_D^{20} −8·02°. Later distillates had lower rotations: (1·23 g.), b. p. 42°/0·5 mm., n_D^{20} 1·4870, α_D^{20} +52·65°; (0·79 g.) (Found: I, 52·5%), b. p. 42°/0·5 mm., n_D^{20} 1·4870, α_D^{20} +41·46° (this may be due to racemisation by the C$_5$H$_5$NHI still present).

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