The Organic Chemistry of Phosphorus. Part II.* The Action of Triphenyl Phosphite Dihalides on Alcohols : Two Further New Methods for the Preparation of Alkyl Halides.

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Alkyl halides may be prepared conveniently and in good yield from triphenyl phosphite, an alcohol, and a halogen, either by adding the halogen to a mixture of the alcohol and the phosphite :

$$(PhO)_3P + ROH + Hal_2 \longrightarrow RHal + Hal \cdot PO(OPh)_2 + PhOH$$

or by first preparing the triphenyl phosphite dihalide and then treating this with the alcohol :

$$(PhO)_3PHal_2 + ROH \longrightarrow RHal + Hal \cdot PO(OPh)_2 + PhOH$$

The results obtained with mixed halogens are described and discussed and the mechanisms of the various reactions are considered briefly.

In Part I * several new methods for the preparation of alkyl halides, based on the overall reaction,

$$(PhO)_3P + ROH + XHal \longrightarrow RHal + X \cdot PO(OPh)_2 + PhOH$$

where X = alkyl, H, NH_4, Na, or Li, were described. In the present paper we describe the extension of this work to the case where X = halogen. As in the previous case, where XHal is an alkyl halide, so also in the present case where XHal is a halogen, the reaction can be carried out either by direct reaction between the three components or by first forming the addition compound of the halogen and the phosphite and treating this with the alcohol; both methods are of preparative value.

Triaryl phosphite dihalides, $(ArO)_3PHal_2$, (triaryloxyhalogenophosphonium halides if electrovalent, or triaryl dihalogenophosphoranetrioates if covalent) have previously been prepared, usually as uncrystallisable oils, by the action of halogen on triaryl phosphites (Noack, *Annalen*, 1883, **218**, 85; Anschütz and Emery, *ibid.*, 1889, **253**, 105; Autenrieth and Geyer, *Ber.*, 1908, **41**, 146; Anschütz, Boedeker, Broeker, and Wenger, *Annalen*, 1927, **454**, 71; Anschütz, Kraft, and Schmidt, *ibid.*, 1939, **542**, 14) and by the action of phosphorus pentahalides on three equivalents of a phenol (Autenrieth and Geyer, *loc. cit.*; Anschütz, Kraft, and Schmidt, *loc. cit.*). We have used the former method and have so obtained triphenyl phosphite dichloride, dibromide, di-iodide, bromo-chloride, bromoiodide, and chloro-iodide as crystalline solids; the dichloride was obtained, analytically pure, as colourless prisms, m. p. 80—81°, by crystallisation from acetone–ether under strictly anhydrous conditions; work at present in progress on the purification of the other dihalides will be reported later.

Triphenyl phosphite dihalides react very readily with alcohols to form alkyl halides, thus :

$$(PhO)_3PHal_2 + ROH \longrightarrow RHal + Hal \cdot PO(OPh)_2 + PhOH$$

That the reaction takes this course, rather than the alternative :

$$(PhO)_3PHal_2 + ROH \longrightarrow RHal + (PhO)_3PO + HHal$$

as suggested by Milobendski and Kolitowska (*Roczn. Chem.*, 1926, **6**, 67), who obtained menthyl chloride by the action of triphenyl phosphite dichloride probably contaminated with phosphorus pentachloride on menthol, is shown by the presence of phenol in the reaction products and the absence of hydrogen halide and by the formation of diphenyl *N*-phenylphosphoramidate, $(PhO)_2PO \cdot NHPh$, by treatment of the reaction product with aniline. The experimental procedure is simple and convenient; the halogen is passed into, or added gradually to, one equivalent of triphenyl phosphite, with cooling and stirring;

* Part I, *J.*, 1953, 2224.

the crude dihalide so formed is treated dropwise, cooling if necessary, with one equivalent of the alcohol and the resulting alkyl halide is then isolated, usually by direct distillation. The reaction residue yields triphenyl phosphate when heated or on treatment with bases :

$$\text{PhOH} + \text{Hal·PO(OPh)}_2 \longrightarrow \text{HHal} + \text{(PhO)}_3\text{PO}$$
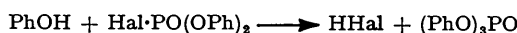
The yields of seven representative alkyl halides varied from 60% to 98%. The reaction proceeds quite satisfactorily with unsaturated alcohols; substantial inversion of configuration occurs with octan-2-ol, but cholesterol yields the uninverted cholesteryl halide (cf. Part I, *loc. cit.*).

An even simpler method involves the direct reaction of the three components :

$$\text{(PhO)}_3\text{P} + \text{ROH} + \text{Hal}_2 \longrightarrow \text{RHal} + \text{Hal·PO(OPh)}_2 + \text{PhOH}$$
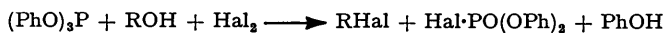
the evidence for this reaction course being similar to that advanced above for the two-component reaction. The experimental procedure is extremely simple and rapid; one equivalent of the halogen is passed into, or added gradually to, a stirred mixture at 0° of one equivalent of the alcohol and one equivalent of triphenyl phosphite; after the reaction mixture has been kept at room temperature for some time, the alkyl halide is isolated by direct distillation or other convenient means. Yields in ten representative cases varied from 62% to 92%, the average being 72%; for obvious reasons this method is not very suitable for the preparation of unsaturated alkyl halides, for which the two-component procedure is quite satisfactory; like the two-component procedure, the method gave very unsatisfactory results with *cyclo*hexanol. This method is the simplest and most convenient of all those using triphenyl phosphite described in this paper and in Part I; in view of the ease and speed with which it may be carried out, the low temperature at which it proceeds, and the commercial availability, at low cost, of triphenyl phosphite, the method may well be preferred to the older and more conventional methods for the preparation of saturated alkyl halides of all kinds; for unsaturated halides, the method using the pre-formed triphenyl phosphite dihalides is the method of choice. If two equivalents of alcohol are used, the initial reaction leads to the formation of a mixed alkyl phenyl phosphorohalidate; such compounds may decompose on being heated to yield a second equivalent of alkyl halide (Balarew, *Z. anorg. Chem.*, 1917, **99**, 187; **101**, 225) :

$$\text{Hal·PO(OR)(OPh)} \longrightarrow \text{RHal} + \text{PhO·PO}_2$$
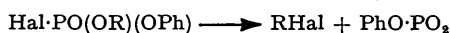
The decomposition temperature of the phosphorochloridates (cf. Gerrard, *J.*, 1940, 1464) and phosphorobromidates is too high for this reaction to be of practical value but the phosphoroiodidates decompose at lower temperatures and a considerable economy in iodine can be achieved in the preparation of *n*-butyl iodide, and presumably of other alkyl iodides, by using two equivalents of the alcohol.

Both of the preparative reactions just discussed can be accommodated within the obvious modification of the general scheme advanced in Part I (*loc. cit.*, p. 2227) for the similar reactions of methyl iodide, which it does not seem necessary to reproduce.

Considerable interest attaches to the course of both reactions when a mixed halogen (halogen halide) is used. The average results of numerous experiments carried out using pre-formed dihalides are given in Table 1. Qualitatively similar results were obtained in

TABLE 1. *Molar ratios of alkyl halides from butyl alcohols and triphenyl phosphite dihalides.*

	(PhO)$_3$PClBr RBr : RCl	(PhO)$_3$PClI RI : RCl	(PhO)$_3$PBrI RI : RBr
n-Butyl alcohol	92 : 8	77 : 23	32 : 68
sec.-Butyl alcohol	100 : 0	75 : 25	21 : 79
tert.-Butyl alcohol	94 : 6	47 : 53	21 : 79

experiments in which iodine chloride was added to mixtures of the three butyl alcohols and triphenyl phosphite, and also in experiments in which *n*-butyl alcohol was treated with some diphenyl trihalogenophosphoranedioates and phenyl tetrahalogenophosphoranoates; the results of the latter experiments were :

	(PhO)$_2$PClBr$_2$	(PhO)$_2$PCl$_2$Br	PhO·PClBr$_3$	PhO·PCl$_2$Br$_2$	PhO·PCl$_3$Br
Molar ratio, Bu^{n}Br : Bu^{n}Cl ...	100 : 0	90 : 10	100 : 0	100 : 0	75 : 25

Experiments were also carried out with optically active octan-2-ol, with results summarised in Table 2.

TABLE 2. *Experiments with octan-2-ol.*

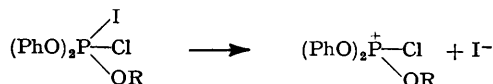| Dihalide	Products		
	Halide	Yield (%)	Inversion (%) *
$(PhO)_3PCl_2$	$C_8H_{17}Cl$	59	90
$(PhO)_3PI_2$	$C_8H_{17}I$	69	23
$(PhO)_3PClBr$ .... {	$C_8H_{17}Br$	73	56
	$C_8H_{17}Cl$	17	32
$(PhO)_3PClI$ .... {	$C_8H_{17}I$	47	65
	$C_8H_{17}Cl$	1	72
$(PhO)_3PBrI$ .... {	$C_8H_{17}I$	14	45
	$C_8H_{17}Br$	39	74

* Calc. from the specific rotations given by Brauns (*Rec. Trav. chim.*, 1946, **65**, 799); 100% indicates complete inversion, 0% complete racemisation.

These results, except those relating to the action of triphenyl phosphite chloro-iodide on *tert.*-butyl alcohol, reveal a marked tendency for the formation of alkyl iodides and bromides in preference to chlorides, whereas alkyl bromides are formed in preference to iodides.

It will be convenient to consider first the results with the chloro-iodide and chloro-bromide. The observed high degree of optical inversion in the reactions with octan-2-ol (cf. the results of Gerrard and Green, *J.*, 1951, 2550, on the Arbusov reaction with tri-2-octyl phosphite) suggests attack on the ester-exchanged intermediate by halide ion (cf. Part I), thus :
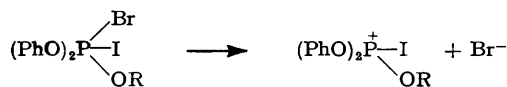
$$(PhO)_3\overset{+}{P}\diagdown\begin{matrix}Hal\\O\!-\!R \quad Hal^-\end{matrix} \longrightarrow (PhO)_2P\diagdown\begin{matrix}Hal\\O\end{matrix} + RHal$$

It follows that, in the compounds under immediate consideration, it is the halogen other than chlorine which ionises, *e.g.* :

$$(PhO)_2P\diagdown\begin{matrix}I\\Cl\\OR\end{matrix} \longrightarrow (PhO)_2\overset{+}{P}\diagdown\begin{matrix}Cl\\OR\end{matrix} + I^-$$

This at first sight appears anomalous, since the more electronegative halogen might have been expected to ionise preferentially, but the case is analogous to the well-known one of the reactivity of the alkyl halides and, like this, finds its explanation in the government of the ionisation by bond strength rather than electronegativity; the P–Cl bond (heat of formation, 77 kcal./mole) is much stronger than the P–Br and the P–I bond (heats of formation, 63·5 and 49·5 kcal./mole, respectively) and it is not unreasonable that the P–Cl linkage should be considerably more reluctant to ionise than the other two.

The results with the bromo-iodide are less easily explained, since here it is apparently the strongest link which ionises, thus :

$$(PhO)_2P\diagdown\begin{matrix}Br\\I\\OR\end{matrix} \longrightarrow (PhO)_2\overset{+}{P}\diagdown\begin{matrix}I\\OR\end{matrix} + Br^-$$

In all such cases of competition for ionisation from a central phosphorus (or other) atom, each halogen will, by virtue of its electron-attracting capacity, reduce the tendency of the other to ionise; our results suggest that the effect of the bromine atom on the ionisation tendency of the iodine is so much greater than the similar effect of the iodine on the bromine as to result in preferential ionisation of the P–Br linkage, in spite of its greater strength; work is in hand with the object of obtaining experimental evidence on this point. The possibility that the reaction might lead initially to alkyl iodide and phosphoro-bromidate, which then undergo halogen exchange, has been excluded by direct experiment. The stereochemical similarity in the reactions of all three mixed dihalides with octan-2-ol at least lends no support to the suggestion that there may be some mechanistic singularity in the reaction with the bromo-iodide. There remains the possibility of some structural

difference between the chlorine-containing dihalides and the others (cf. phosphorus penta-chloride and phosphorus pentabromide); this, too, we intend to investigate.

Experiments were also carried out on the action of bromine, iodine, iodine chloride, and iodine bromide on tri-*n*-butyl phosphite; the results (p. 2288) are difficult to interpret, since appreciably more than one mole of alkyl halide is formed, the second mole arising from decomposition of the dibutyl phosphorohalidate formed in the first stage of the reaction.

EXPERIMENTAL

(Rotations were determined without solvent in 1-dm. tubes.)

Preparation of Triphenyl Phosphite Dihalides.—These compounds are readily prepared by the direct action of halogens or mixed halogens on triphenyl phosphite with the rigorous exclusion of moisture. In the case of chlorine, the dried gas was passed into the phosphite, with cooling and stirring, until the theoretical amount had been taken up; with bromine and iodine chloride, the required amount of the halogen was added dropwise to the cooled and stirred phosphite; in the case of bromine chloride, the phosphite was slowly added to the halogen cooled to $-40°$; the di-iodide and bromo-iodide were prepared by adding the theoretical amount of powdered halogen to triphenyl phosphite and stirring the mixture over-night at room temperature. Although all the dihalides were obtained as crystalline solids, only the dichloride was further purified; the crude dihalides are quite suitable for reaction with alcohols.

Triphenyl phosphite dichloride. The crude dichloride (0·1 mole), prepared in liquid form by passing chlorine into triphenyl phosphite with slight cooling, was stirred vigorously with light petroleum (b. p. 60—80°; 100 ml.) and then with ether, whereupon it solidified to glistening colourless prisms, which were washed with ether by decantation. For recrystallisation, the compound, as a thick slurry in dry ether, was dissolved in the minimum amount of cold, dry acetone and then precipitated, as fine colourless prisms, by the addition of dry ether ($\frac{1}{2}$ vol.) with vigorous stirring. After decantation of the solvent and washing of the crystals with ether, the process was repeated until the m. p. was constant; the *dichloride (chlorotriphenoxy-phosphonium chloride* or *triphenyl dichlorophosphoranetrioate*) has m. p. 80—81° (Found : Cl, 18·0. $C_{18}H_{15}O_3PCl_2$ requires Cl, 18·6%).

Preparation of Alkyl Halides from Triphenyl Phosphite Dihalides.—(a) n-*Butyl chloride.* *n*-Butyl alcohol (11 g.) was added dropwise to crude triphenyl phosphite dichloride (from triphenyl phosphite, 50 g.) at room temperature; the reaction was completed by gentle warming and the product distilled under reduced pressure into traps cooled to $-80°$. Distillation, washing of the fraction of b. p. 78—79° with water, drying, and redistillation afforded *n*-butyl chloride (10·5 g., 76%), b. p. 78—79°, n_D^{21} 1·4015.

(b) cyclo*Hexyl chloride.* *cyclo*Hexanol (15 g.) was added slowly to the dichloride from triphenyl phosphite (51 g.), and the mixture kept overnight at room temperature. Two distil-lations gave *cyclo*hexyl chloride (6·1 g., 34%), b. p. 90—95°/65 mm., n_D^{22} 1·4612.

(c) *Allyl bromide.* Allyl alcohol (5·8 g.) was added slowly to the dibromide from triphenyl phosphite (34 g.), with cooling. After the vigorous reaction had abated, the mixture was distilled under reduced pressure into traps cooled to $-80°$. Redistillation of the washed condensate gave allyl bromide (9 g., 75%), b. p. 70—72°, n_D^{26} 1·4650. Dimethylaniline (6 g.) was added cautiously to the residue from the original distillation; the product was kept at room temperature for an hour and then treated with ether (250 ml.). After being washed with 10% methanol, 2N-sodium hydroxide, and water, the dried solution was evaporated and the solid residue of crude triphenyl phosphate (32 g., 98%; m. p. 39°) recrystallised from light petroleum (b. p. 40—60°), yielding the pure phosphate as long needles, m. p. and mixed m. p. 47°.

(d) *Cholesteryl bromide.* Cholesterol (2 g.) was added to the dibromide from triphenyl phosphite (6 g.) and the mixture warmed at 60—70° for 15 min. The product was diluted with acetone (50 ml.) and cooled; cholesteryl bromide (1·4 g.; m. p. 86—90°) separated in platelets and a further crop (0·8 g.; m. p. 89—90°) was obtained by diluting the filtrate with water. Two recrystallisations from ethyl acetate gave the pure bromide, m. p. 97—98° (Found : Br, 18·05. Calc. for $C_{27}H_{45}Br$: Br, 17·8%).

(e) n-*Butyl iodide.* *n*-Butyl alcohol (7·4 g.) was slowly added to the di-iodide from triphenyl phosphite (34 g.). After the vigorous reaction had abated, the product was distilled under reduced pressure into traps at $-80°$; washing and redistillation gave *n*-butyl iodide (16 g.,

87%), b. p. 129—131°, n_D^{23} 1·4980. The residue from the initial distillation was heated at 250° for 3 hr. and then dissolved in ether (100 ml.) and washed with 10% methanol, 2N-sodium hydroxide, and water. Evaporation of the dried extract gave triphenyl phosphate (25 g., 70%), m. p. 37° raised to 46° by recrystallisation from light petroleum (b. p. 40—60°).

(f) *tert.-Butyl iodide.* *tert.*-Butyl alcohol (8 g.) was added dropwise to the di-iodide from triphenyl phosphite (34 g.), and the mixture was kept at room temperature for 30 min. Two distillations gave *tert.*-butyl iodide (15 g., 83%), b. p. 95°, n_D^{20} 1·4890.

Preparation of Alkyl Halides from Triphenyl Phosphite, Halogens, and Alcohols.—The appropriate halogen was added dropwise to, or passed into, a stirred mixture of the alcohol and triphenyl phosphite at 0°. After being kept at room temperature for some time, the crude alkyl halide was distilled from the reaction mixture under reduced pressure, washed, dried, and re-distilled.

Preparative experiments, on the 0·1-molar scale, are summarised in Table 3.

TABLE 3. *Alkyl halides from triphenyl phosphite, halogens, and alcohols.*

Reactants (and molar ratio)	Reaction time (hr.)	Product		
		Yield (% ; based on alcohol)	B. p.	n_D^{20}
Bu^{n}OH, Cl$_2$, (PhO)$_3$P (2 : 1 : 1)	2	Bu^{n}Cl, 49	—	1·4050
Bu^{n}OH, Br$_2$, (PhO)$_3$P (1 : 1 : 1) [1]	1	Bu^{n}Br, 80	100—101°	1·4400
Bu^{n}OH, Br$_2$, (PhO)$_3$P (2 : 1 : 1)	3	Bu^{n}Br, 58	—	1·4403
Bu^{n}OH, I$_2$, (PhO)$_3$P (2 : 1 : 1) [2]	2	Bu^{n}I, 75	123—126°	1·5001
Bu^{n}OH, ICl, (PhO)$_3$P (1 : 1 : 1)	1	Bu^{n}Cl, 23 ; Bu^{n}I, 65	—	1·4749
Bu^{r}OH, ICl, (PhO)$_3$P (1 : 1 : 1)	1	Bu^{s}Cl, 14 ; Bu^{s}I, 61	—	1·4762
Bu^{t}OH, Cl$_2$, (PhO)$_3$P (1 : 1 : 1)	1	Bu^{t}Cl, 62	54°	1·4018
Bu^{t}OH, Br$_2$, (PhO)$_3$P (1 : 1 : 1) [3]	1	Bu^{t}Br, 76	70°	1·4283
Bu^{t}OH, Br$_2$, (C$_7$H$_8$O)$_3$P (1 : 1 : 1) [4] ...	1	Bu^{t}Br, 85	72°	1·4300 (n_D^{18})
Bu^{t}OH, ICl, (PhO)$_3$P (1 : 1 : 1)	1	Bu^{t}Cl, 39 ; Bu^{t}I, 46	—	1·4420
HO·[CH$_2$]$_3$·OH, Cl$_2$, (PhO)$_3$P (1 : 2 : 1)	1	Cl·[CH$_2$]$_3$·Cl, 63	70—73°/50 mm.	1·4470
HO·[CH$_2$]$_3$·OH, Br$_2$, (PhO)$_3$P (1 : 2 : 1) [5]	1	Br·[CH$_2$]$_3$·Br, 92	90°/80 mm.	1·5250
Et lactate, Cl$_2$, (PhO)$_3$P (1 : 1 : 1)	1	Et α-chloropropionate, 79	70°/60 mm.	1·4209 (n_D^{14})
Et lactate, Br$_2$, (PhO)$_3$P (1 : 1 : 1) ...	1	Et α-bromopropionate, 82	70°/30 mm.	1·4460
Ph·CH$_2$·CH$_2$·OH, Cl$_2$, (PhO)$_3$P (1 : 1 : 1)	1	Ph·CH$_2$·CH$_2$Cl, 78	105°/20 mm.	1·5273
Ph·CH$_2$·CH$_2$·OH, Br$_2$, (PhO)$_3$P (1 : 1 : 1)	1	Ph·CH$_2$·CH$_2$Br, 82	120°/10 mm.	1·5570

[1] Distillation of the residue gave a 53% yield of triphenyl phosphate. [2] The alcohol and phosphite were heated for 90 min. at 100° before addition of the iodine. [3] The residue was dissolved in ether (50 ml.), shaken with 100-ml. portions of 10% sodium hydroxide, 10% methanol, and water, dried, and evaporated ; crystallisation of the residue from light petroleum (b. p. 40—60°) gave triphenyl phosphate (15·5 g., 48%), m. p. 47°. [4] Tri-*p*-tolyl phosphite (Michaelis and Kähne, *Ber.*, 1898, 31, 1048) was used in this experiment. [5] Distillation of the residue gave a 45% yield of triphenyl phosphate.

Formation of Diphenyl Phosphorohalidates.—Bromine (16·2 g., 0·1 mole) was added dropwise, with stirring, to an ice-cooled mixture of triphenyl phosphite (34 g., 0·11 mole) and *tert.*-butyl alcohol (7·4 g., 0·1 mole). The mixture was kept at room temperature for 1 hr. and aniline (24 g., 0·25 mole) was then added rapidly with vigorous stirring; after 48 hr., the mixture was heated at 100° for 30 min. and then steam-distilled to remove phenol and excess of aniline. The organic part of the residue solidified (m. p. 115—120°) and was identified as diphenyl *N*-phenylphosphoramidate (25·5 g., 70%) by crystallisation from ethanol (m. p. 130—131°; lit., m. p. 129—130°) (Found : N, 4·45. Calc. for C$_{18}$H$_{16}$O$_3$NP : N, 4·3%). The same compound was obtained similarly from the products of the action of iodine chloride on a mixture of triphenyl phosphite and *n*-butyl alcohol and of the action of triphenyl phosphite bromoiodide on *tert.*-butyl alcohol.

Action of Triphenyl Phosphite Dihalides on Butyl Alcohols.—The dihalide (0·2 mole), prepared in the usual manner, was kept for the time specified in Table 4, and the alcohol (0·2 mole) then added slowly, stirring being recommenced as soon as the mixture was sufficiently fluid. After completion of the addition, the mixture was set aside at room temperature for an hour and then distilled under reduced pressure into traps cooled to −80°, distillation being stopped when phenol began to distil over. The distillate was twice washed with 2N-sodium hydroxide and with water and finally dried (Na$_2$SO$_4$) ; the composition of the product was estimated from the refractive index and the refractive indices of the pure components determined at the same time. The results are summarised in Table 4.

Action of Diphenyl Trihalogenophosphoranedioates and Phenyl Tetrahalogenophosphoranoates on n-Butyl Alcohol.—(a) *Diphenyl dibromochlorophosphoranedioate.* Bromine (32 g., 0·2 mole)

was added dropwise, with cooling and stirring, to diphenyl phosphorochloridite (50·5 g.,) 0·2 mole) (b. p. 144—158°/2 mm.; n_D^{24} 1·5774; Noack, *Annalen*, 1883, **218**, 85); after the addition compound had solidified it was kept at room temperature for an hour. *n*-Butyl alcohol (15 g., 0·2 mole) was then added, with cooling, stirring being recommenced as soon as possible. Isolation of the product in the usual manner gave *n*-butyl bromide (24 g., 87%), n_4^{20} 1·4400, essentially free from the chloride.

TABLE 4. *Action of triphenyl phosphite dihalides on butyl alcohols.*

Reactants Alcohol, ROH	Dihalide	Period of keeping of dihalide before reaction (hr.)	Products (yield, %) RCl	RBr	RI	Molar ratio of products	Mean molar ratio of products
Bu^nOH	(PhO)₃PClBr	0·5	8	86	—	9 : 91	
,,	,,	1	11	87	—	11 : 89	
,,	,,	18	0	94	—	0 : 100	8 : 92
,,	,,	*	12	88	—	12 : 88	
,,	(PhO)₃PClI	0·5	21	—	58	27 : 73	
,,	,,	1	19	—	74	20 : 80	
,,	,,	1	21	—	74	22 : 78	
,,	,,	18	17	—	70	20 : 80	23 : 77
,,	,,	18 (100°)	18	—	67	21 : 79	
,,	,,	19	24	—	59	29 : 71	
,,	,,	120	19	—	72	21 : 79	
,,	(PhO)₃PBrI	0·5	—	62	35	64 : 36	
,,	,,	1	—	54	28	66 : 34	
,,	,,	1	—	64	30	68 : 32	
,,	,,	2	—	65	35	65 : 35	68 : 32
,,	,,	18	—	60	25	71 : 29	
,,	,,	18	—	65	23	74 : 26	
,,	,,	40	—	64	27	70 : 30	
Bu^sOH	(PhO)₃PClBr	1·5	0	87	—	0 : 100	0 : 100
,,	,,	18	0	92	—	0 : 100	
,,	(PhO)₃PClI	0·5	22	—	54	29 : 71	
,,	,,	1	12	—	68	15 : 85	25 : 75
,,	,,	18	23	—	53	30 : 70	
,,	(PhO)₃PBrI	1	—	60	26	70 : 30	
,,	,,	1	—	76	20	79 : 21	
,,	,,	18	—	68	20	77 : 23	79 : 21
,,	,,	60	—	86	11	89 : 11	
Bu^tOH	(PhO)₃PClBr	1	0	91	—	0 : 100	7 : 93
,,	,,	60	12	79	—	13 : 87	
,,	(PhO)₃PClI	1	46	—	39	54 : 46	
,,	,,	1	37	—	44	46 : 54	
,,	,,	1	38	—	31	55 : 45	53 : 47
,,	,,	18	51	—	47	52 : 48	
,,	,,	24	46	—	34	57 : 43	
,,	(PhO)₃PBrI	0·5	—	76	16	83 : 17	
,,	,,	1	—	68	19	78 : 22	
,,	,,	18	—	67	22	75 : 25	79 : 21
,,	,,	18	—	75	15	83 : 17	
,,	,,	21	—	61	17	78 : 22	

* Chlorine (0·05 mole) was passed into triphenyl phosphite (0·1 mole); bromine (0·05 mole) was then added and the mixture heated at 100° for 20 min. After cooling, the reaction was carried out as usual.

(b) *Diphenyl bromodichlorophosphoranedioate.* Diphenyl phosphorochloridite (50·5 g., 0·2 mole) was added very cautiously to bromine chloride (23 g., 0·2 mole) at −70° and the resulting addition compound treated with *n*-butyl alcohol (15 g., 0·2 mole). The product (22·2 g.; n_D^{20} 1·4354) was a mixture of *n*-butyl chloride (1·9 g., 10%) and *n*-butyl bromide (20·3 g., 74%).

(c) *Phenyl bromotrichlorophosphoranoate.* Phenyl phosphorodichloridite (39 g., 0·2 mole; b. p. 57—58°/2 mm., n_D^{25} 1·5578; Noack, *loc. cit.*) was added cautiously to bromine chloride (23 g., 0·2 mole), and the resulting addition compound treated with *n*-butyl alcohol (15 g., 0·2 mole). The product (15 g.; n_D^{20} 1·4315) was a mixture of *n*-butyl chloride (13% yield) and *n*-butyl bromide (46% yield).

(d) *Phenyl dibromodichlorophosphoranoate.* Bromine (32 g., 0·2 mole) was added to phenyl phosphorodichloridite (39 g., 0·2 mole), and the resulting addition compound treated with *n*-butyl alcohol (15 g., 0·2 mole); much hydrogen chloride was evolved and an additional amount of *n*-butyl alcohol (2 g.) had to be added to complete the dissolution of the addition

compound. The halide formed, isolated in the usual manner, was essentially pure *n*-butyl bromide (25 g., 91%), n_D^{20} 1·4403. The residue from the initial distillation was treated with an excess of aniline; steam-distillation left a solid (35 g.), which, on repeated crystallisation from ethanol and chromatography on alumina in benzene–chloroform (1 : 1), yielded phenyl *NN'*-diphenylphosphorodiamidate, m. p. 177—178° (Audrieth and Toy, *J. Amer. Chem. Soc.*, 1942, **64**, 1337, give m. p. 179—180°) (Found : C, 67·7; H, 5·4; N, 8·2. Calc. for $C_{18}H_{17}O_2N_2P$: C, 66·7; H, 5·25; N, 8·6%).

(e) *Phenyl tribromochlorophosphoranoate.* Phenyl phosphorodibromidite (57 g., 0·2 mole; b. p. 125—130°/11 mm.; Strecker and Grossmann, *Ber.*, 1916, **49**, 63) was added cautiously to bromine chloride (23 g., 0·2 mole) at −70° and the resulting addition compound treated with *n*-butyl alcohol (15 g., 0·2 mole). Hydrogen halide was evolved and it was necessary to add more *n*-butyl alcohol (1·5 g.) to complete the dissolution of the addition compound. Working up in the usual manner gave essentially pure *n*-butyl bromide (28 g., 100%), n_D^{20} 1·4402.

Action of Triphenyl Phosphite Dihalides on Octan-2-ol.—Octan-2-ol was resolved by the method of Pickard and Kenyon (*J.*, 1907, **91**, 2058); the triphenyl phosphite dihalides were prepared by slowly adding the appropriate halogen to cooled, stirred triphenyl phosphite and keeping the mixture for 24 hr. The dihalide was then treated, with cooling and stirring, with octan-2-ol, and the mixture was set aside for 30 min. and then distilled under reduced pressure into traps cooled to −70°. The distillate was dissolved in ether, washed with sodium hydroxide and water, dried (Na_2SO_4), and distilled.

The composition of each fraction was determined from its refractive index. In every case one fraction consisted of a pure halide and it was thus possible, by using the observed rotation of this fraction, to calculate the rotation of the other halide present in the other fractions from the observed rotations; the rotations given for this second halide are the means of the values calculated in this way.

Triphenyl phosphite dichloride. (+)-Octan-2-ol (13 g.; $[\alpha]_D^{21}$ +8·72°) gave (−)-2-chloro-octane (8·7 g., 59%), b. p. 59°/13 mm., n_D^{20} 1·4265, $[\alpha]_D^{21}$ −28·67°.

Triphenyl phosphite di-iodide. (−)-Octan-2-ol (13 g.; $[\alpha]_D^{27}$ −8·65°) gave (+)-2-iodo-octane (16·6 g., 69%), b. p. 42°/0·5 mm., n_D^{20} 1·4881, $[\alpha]_D^{23}$ +9·53°.

Triphenyl phosphite chlorobromide. (−)-Octan-2-ol (11·7 g.; $[\alpha]_D^{21}$ −9·24°) gave the following fractions : (i) b. p. 46—85°/30 mm., 1·1 g., n_D^{20} 1·4262, $[\alpha]_D^{22}$ +10·90°; (ii) b. p. 85°/30 mm., 2·0 g., n_D^{20} 1·4430, α_D^{22} +21·49°; (iii) b. p. 85—87°/30 mm., 5·2 g., n_D^{20} 1·4468, $[\alpha]_D^{22}$ +22·08°; (iv) b. p. 87°/20 mm., 4·5 g., n_D^{20} 1·4510, α_D^{22} +20·98°; (v) b. p. 87—95°/20 mm., 2·3 g., n_D^{20} 1·4502, α_D^{22} +20·90°. Fraction (i) was practically pure 2-chloro-octane, and fractions (iv) and (v) were somewhat impure 2-bromo-octane. Calculation showed the whole product to contain 2·3 g. (17% yield) of (+)-2-chloro-octane, $[\alpha]_D^{22}$ +10·9°, and 12·7 g. (73% yield) of (+)-2-bromo-octane, $[\alpha]_D^{22}$ +21·2°.

Triphenyl phosphite chloro-iodide. (+)-Octan-2-ol (20 g.; $[\alpha]_D^{22}$ +8·72°) yielded 16·5 g. of almost pure (−)-2-iodo-octane, n_D^{20} 1·4868, $[\alpha]_D^{23}$ −27·46°. On distillation, the first few drops (0·75 g.) which contained all the chloro-octane, had n_D^{20} 1·4569, α_D^{23} −24·78°. Calculation showed that the whole product contained 16·2 g. (47% yield) of (−)-2-iodo-octane, $[\alpha]_D^{23}$ −27·5°, and 0·3 g. (1% yield) of (−)-2-chloro-octane, $[\alpha]_D^{23}$ −23·0°.

Triphenyl phoshite bromo-iodide. (−)-Octan-2-ol (20 g.; $[\alpha]_D^{22}$ −8·81°) gave : (i) b. p. 81—82°/19 mm., 8·7 g., n_D^{23} 1·4500, α_D^{20} +29·56°; (ii) b. p. 82—84°/22 mm., 6·0 g., n_D^{23} 1·4548, α_D^{20} +29·28°; (iii) b. p. 84—86°/22 mm., 4·0 g., n_D^{23} 1·4769, α_D^{20} +25·42°; (iv) b. p. 98—110°/22 mm., 3·0 g., discoloured by iodine. Calculation showed the whole product to contain 15·1 g. (39% yield) of (+)-2-bromo-octane, $[\alpha]_D^{20}$ +26·75°, and 6·6 g. (14% yield) of (+)-2-iodo-octane, $[\alpha]_D^{20}$ +19·25°.

Attempted Exchange Reactions.—n-*Butyl chloride and diphenyl phosphorobromidate.* The dibromide from triphenyl phosphite (62 g., 0·2 mole) was treated, as usual, with anhydrous methanol (6·4 g., 0·2 mole), and the mixture stirred for an hour. After removal of the methyl bromide under reduced pressure, *n*-butyl chloride (18·4 g., 0·2 mole) was added to the residual mixture of phenol and diphenyl phosphorobromidate. The mixture was kept for 75 min. at room temperature; distillation, washing, and redistillation gave only *n*-butyl chloride (16·5 g., 90%) b. p. 72°, n_D^{20} 1·4020.

n-*Butyl iodide and diphenyl phosphorobromidate.* Repetition of the above experiment, with *n*-butyl iodide (35 g.) in place of the chloride, similarly gave only recovered *n*-butyl iodide (29·5 g., 85%), n_D^{20} 1·4945.

Action of Halogens on Tri-n-butyl Phosphite.—The halogen (0·1 mole) was added dropwise, with stirring, to ice-cooled tri-*n*-butyl phosphite (0·1 mole; b. p. 105—110°/0·5 mm., n_D^{25} 1·4303;

Gerrard, *J.*, 1940, 1464). After 3 hr. at room temperature the product was distilled under reduced pressure into traps cooled to $-70°$, all material boiling below $100°/20$ mm. being collected. The distillate was washed with 10% sodium hydroxide solution and water and dried ($MgSO_4$). The results were :

Halogen	n_D^{20}	Product Yield (mole) Bu^{n}Br	Bu^{n}I	Halogen	n_D^{20}	Product Yield (mole) Bu^{n}Cl	Bu^{n}Br	Bu^{n}I
Br$_2$	1·4389	0·20	—	ICl	1·4731	0·035	—	0·09
I$_2$	1·4935	—	0·19	IBr	1·4760	—	0·07	0·10

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