590. *The Organic Chemistry of Phosphorus. Part III.* The Nature of the Compounds of Triaryl Phosphites and the Halogens.*

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The reaction between triphenyl phosphite and halogens has been shown to proceed in several stages, the first two of which may be represented as:

$$(\alpha)\ 2(PhO)_3P + Hal_2 \longrightarrow (PhO)_2PHal + (PhO)_4PHal$$

$$(\beta)\ (PhO)_2PHal + (PhO)_4PHal + Hal_2 \longrightarrow 2(PhO)_3PHal_2$$

The second stage may be followed by exchange of cations and anions among the dimeric forms of the triphenoxy-dihalide with the formation of all or any of the possible phenoxy-halides, $(PhO)_nPHal_{5-n}$.

Studies of the hydrolysis and alcoholysis of various products prepared in this way, and by the action of phosphorus pentachloride on phenol, indicate that the phenoxy-chlorides and -bromides are the dimeric polyhalogenopolyphenoxyphosphonium polyphenoxypolychlorophosphates,† $[(PhO)_xPHal_{4-x}]^+[(PhO)_yPHal_{6-y}]^-$, or mixtures of such compounds, whereas the iodides are the monomeric phosphonium compounds, $[(PhO)_nPI_{4-n}]^+I^-$.

In 1883 Noack [1] prepared triphenoxyphosphorus dibromide, $(PhO)_3PBr_2$, by the addition of bromine to triphenyl phosphite. Since then, many aryloxyphosphorus halides of the general formula, $(ArO)_nPHal_{5-n}$, have been prepared,[2] both by the addition of halogens to triaryl phosphites, diaryl phosphorohalidites, or aryl phosphorodihalidites and by the action of phosphorus pentachloride on phenols. The earlier workers described most of these substances as oils or unstable liquids but, in 1954, Coe, Landauer, and Rydon [3] obtained six of the triphenoxyphosphorus dihalides or "triphenyl phosphite dihalides," $(PhO)_3PHal_2$, as crystalline solids.

In continuing this work we had little difficulty in obtaining nine such compounds [*viz.*, the six "triphenyl phosphite dihalides," $(PhO)_3PHal_2$, where $Hal_2 = Cl_2$, Br_2, I_2, BrCl, ClI, and BrI, and three "tri-2 : 6-xylyl phosphite dihalides," ‡ $(2:6\text{-}Me_2C_6H_3O)_3PHal_2$, where $Hal_2 = Cl_2$, Br_2, and I_2] as apparently well-defined crystalline solids, giving correct halogen analyses and having definite melting points. However, in attempts to prepare highly purified specimens of certain of these compounds for conductivity and *X*-ray crystallographic work, it became apparent that these compounds were less stable and more complex in structure than appeared at first sight. In particular, the halogen content frequently fell on repeated recrystallisation [*e.g.*, the dibromide, $(PhO)_3PBr_2$, finally yielded a product appearing from analysis to be the tetraphenoxy-bromide, $(PhO)_4PBr$], while treatment with water afforded appreciable quantities of phenol; abnormal hydrolysis

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* Part II, Coe, Landauer, and Rydon, *J.*, 1954, 2281.

† No authoritive nomenclature exists for ions of the type PY_6^-. The organic nomenclature makes no provision for such anions and we have accordingly used the tentative I.U.P.A.C. inorganic nomenclature rules in this paper; we are indebted to the Editor for this suggestion.

‡ In 2 : 6-xylyl, etc., the point of attachment (to oxygen) is numbered 1 (cf. *J.*, 1952, 5091, footnote 22).

[1] Noack, *Annalen*, 1883, **218**, 85.

[2] Anschütz and Emery, *ibid.*, 1887, **239**, 301; 1889, **253**, 105; Autenrieth and Geyer, *Ber.*, 1908. **41**, 146; Anschütz, Boedeker, Broeker, and Wenger, *Annalen*, 1927, **454**, 71; Anschütz and Wenger, *ibid.*, 1930, **482**, 25; Anschütz, Koenig, Otto, and Walbrecht, *ibid.*, 1936, **525**, 297; Anschütz, Kraft, and Schmidt, *ibid.*, 1939, **542**, 14.

[3] Coe, Landauer, and Rydon, *J.*, 1954, 2281.

of the phenoxy-tetrachloride, $PhO{\cdot}PCl_4$, with the formation of triphenyl phosphate, was observed by Anschütz, Koenig, Otto, and Walbrecht[2] but has been ascribed[4] to disproportionation accompanying the hydrolysis. It was clearly necessary to investigate more closely both the structures of these compounds and the course of the reactions by which they are formed from triaryl phosphite and halogens; the present paper is mainly concerned with these studies.

It may be said at once that the reaction between triphenyl phosphite and one mol. of a halogen proceeds in two well-defined stoicheiometric stages; in the first, one mol. of halogen reacts with two of the phosphite and, in the second, a further mol. of halogen reacts with the products of the first stage. The first indication that this was so came from the conductometric experiments of Harris and Payne,[5] who found a marked discontinuity after one mol of bromine had been added to two of triphenyl phosphite in acetonitrile solution; their results further indicated that two ions had been formed at this stage and that no increase in the number of ions accompanied the addition of a further mol. of bromine. Investigation of the products formed from two mols. of triphenyl phosphite and one of bromine in chlorobenzene solution showed them to be diphenyl phosphorobromidite, $(PhO)_2PBr$, isolated by distillation and characterised as the anilide, $(PhO)_2P{\cdot}NHPh$, and the tetraphenoxy-monobromide, $(PhO)_4PBr$, isolated as a crystalline solid giving the correct bromine analysis. Exactly similar results were obtained with chlorine and iodine and the reaction may be generalised, thus:

$$2(PhO)_3P + Hal_2 \longrightarrow (PhO)_2PHal + (PhO)_4PHal \quad . \; . \; . \; . \; . \quad (i)$$

In all three cases the solution remains colourless until this stage is reached, after which colour appropriate to the halogen develops. All three tetraphenoxy-halides may be prepared conveniently by this procedure; the iodide may also be prepared by treatment of the chloride or bromide with methyl iodide, *e.g.*:

$$(PhO)_4PCl + MeI \longrightarrow (PhO)_4PI + MeCl$$

These monohalides may have some advantages over the dihalides previously employed[3] for the preparation of alkyl halides.

The mechanism of reaction (i) is obscure. It seems probable that the dihalide is first formed and then exchanges one of its halogens for a phenoxy-group from a second phosphite molecule to yield the observed products, according to the following equations or their ionic equivalents:

$$(PhO)_3P + Hal_2 \longrightarrow (PhO)_3PHal_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (ia)$$

$$(PhO)_3PHal_2 + (PhO)_3P \longrightarrow (PhO)_4PHal + (PhO)_2PHal \quad . \; . \; . \; . \quad (ib)$$

There is some evidence that the reaction between chlorine and diphenyl phosphorochloridite involves an analogous stage:

$$2(PhO)_2PCl + Cl_2 \longrightarrow (PhO)_3PCl_2 + PhO{\cdot}PCl_2$$

There are numerous possibilities for the further reaction of the products of reaction (i) with halogen. In a solvent of sufficient ionising power the addition may take the following course in which, in agreement with the findings of Harris and Payne,[5] there is no increase in the number of ions:

$$[(PhO)_4P]^+ + Hal^- + (PhO)_2PHal + Hal_2 \longrightarrow [(PhO)_4P]^+ + [(PhO)_2PHal_4]^- \quad . \; . \quad (iia)$$

In a non-ionising solvent this second stage may take the covalent form:

$$(PhO)_4PHal + (PhO)_2PHal + Hal_2 \longrightarrow (PhO)_4PHal + (PhO)_2PHal_3 \quad . \; . \quad (iib)$$

Halogen transfer may then give rise to the ions $[(PhO)_4P]^+$ and $[(PhO)_2PHal_4]^-$ (cf. ii*a*) or exchange of halogen and phenoxy (cf. i*b*) to the covalent form of the triphenoxy-dihalide,

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[4] Kosolapoff, "Organophosphorus Compounds," Wiley, New York, 1950, p. 328.
[5] Harris and Payne, preceding paper.

$(PhO)_3PHal_2$. In either case the covalent triphenoxy-dihalide may be expected to be in equilibrium with all or any of the six possible ionic forms, *viz.*, the monomeric $[(PhO)_3PHal]^+Hal^-$ and the five dimeric * forms ranging from $[(PhO)_4P]^+[(PhO)_2PHal_4]^-$ to $[PHal_4]^+[(PhO)_6P]^-$. Exchange of anions and cations among these six compounds can give rise to other compounds containing less or more halogen than the dihalide, *e.g.*:

$$[(PhO)_4P]^+[(PhO)_2PHal_4]^- + [(PhO_2)PHal_2]^+[(PhO)_4PHal_2]^- \longrightarrow [(PhO)_4P]^+[(PhO)_4PHal_2]^- + [(PhO)_2PHal_2]^+[(PhO)_2PHal_4]^-$$

These again will be in equilibrium with others. The system may thus contain all or any of the 35 possible dimeric compounds of the general formula $[PX_4]^+[PY_6]^-$ derived by combining any of the five cations:

$[(PhO)_4P]^+$ (I)
$[(PhO)_3PHal]^+$ (II)
$[(PhO)_2PHal_2]^+$ (III)
$[PhO{\cdot}PHal_3]^+$ (IV)
$[PHal_4]^+$ (V)

with any of the seven anions:

$[PHal_6]^-$ (VI)
$[PhO{\cdot}PHal_5]^-$ (VII)
$[(PhO)_2PHal_4]^-$ (VIII)
$[(PhO)_3PHal_3]^-$ (IX)
$[(PhO)_4PHal_2]^-$ (X)
$[(PhO)_5PHal]^-$ (XI)
$[(PhO)_6P]^-$ (XII)

and the ten possible monomers, $[PX_4]^+Y^-$, derived by combining the cations (I)—(V) with the halide or phenoxide anions. The actual species present in solution will depend on such factors as temperature and concentration and on the ionising and solvating properties of the solvent, while solubility will play a major part in determining the nature of the solid phase separating from solution. It is thus not surprising that the reaction products of triphenyl phosphite and halogens,† isolated in different ways, have mostly proved to be mixtures of several of the possible compounds in different proportions.

The principal method we have used for the elucidation of the nature of the products, of empirical formula $(PhO)_nPHal_{5-n}$, obtained by treating triphenyl phosphite with halogen and by the action of phosphorus pentachloride on phenol, has been the study of their hydrolysis; the material under investigation was treated with an excess of water, and the following hydrolysis products were determined: (i) halide ion, (ii) triphenyl phosphate, (iii) phenol, and (iv) hydrogen ion by titration to pH 3—5 (HHal, Ph_2HPO_4, PhH_2PO_4, and H_3PO_4 all titrating as monobasic acids).

The hydrolytic behaviour of the five possible cations, $[(PhO)_nPHal_{4-n}]^+$, is expressed in the following five equations:

$$\text{(I)} + H_2O \longrightarrow (PhO)_3PO + PhOH + H^+$$

$$\text{(II)} + H_2O \longrightarrow (PhO)_3PO + Hal^- + 2H^+$$

$$\text{(III)} + 2H_2O \longrightarrow (PhO)_2PO{\cdot}O^- + 2Hal^- + 4H^+$$

$$\text{(IV)} + 3H_2O \longrightarrow PhO{\cdot}PO(OH){\cdot}O^- + 3Hal^- + 5H^+$$

$$\text{(V)} + 4H_2O \longrightarrow H_2PO_4^- + 4Hal^- + 6H^+$$

The hydrolytic behaviour of the ten possible monomeric compounds, $[PX_4]^+Y^-$, is obtained by adding the appropriate anion (Hal^- or PhO^-) to the two sides of these equations, while that of the 35 dimeric compounds, $[PX_4]^+[PY_6]^-$, is obtained by combining the equation

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* Experimental evidence for the occurrence of such dimeric ionic structures is presented later (p. 3049).

† The halogen-transfer reactions involved in the formation of these products are, of course, not likely to be encountered with the products from alkyl phosphites and halogens, since in these the electrophilic reactivity of the alkyl groups will generally lead preferentially to attack by halide ion, with consequent formation of alkyl halides (see, *e.g.*, the earlier parts of this series[3, 6]).

[6] Landauer and Rydon, *J.*, 1953, 2224.

for the cation with one of the following, which express the hydrolytic behavior of the seven anions, $[(PhO)_nPHal_{6-n}]^-$:

$$\begin{aligned}
&(VI) + 4H_2O \longrightarrow H_2PO_4^- + 6Hal^- + 6H^+ \\
&(VII) + 3H_2O \longrightarrow PhO{\cdot}PO(OH){\cdot}O^- + 5Hal^- + 5H^+ \\
&(VIII) + 2H_2O \longrightarrow (PhO)_2PO{\cdot}O^- + 4Hal^- + 4H^+ \\
&(IX) + H_2O \longrightarrow (PhO)_3PO + 3Hal^- + 2H^+ \\
&(X) + H_2O \longrightarrow (PhO)_3PO + PhOH + 2Hal^- + H^+ \\
&(XI) + H_2O \longrightarrow (PhO)_3PO + 2PhOH + Hal^- \\
&(XII) + 2H_2O \longrightarrow (PhO)_3PO + 3PhOH + OH^-
\end{aligned}$$

It should be noted that several structures show identical behaviour on hydrolysis.

The experimental yields of the various hydrolysis products were then compared with those calculated for various binary mixtures of the ten possible monomeric compounds and for similar mixtures of the 35 possible dimeric compounds, the product under consideration being concluded to be that mixture for which the sum of the squares of the differences between theory and experiment was minimal; an abbreviated calculation for one typical case is set out in the Appendix (p. 3055). In nearly every case one mixture fitted the results better than any other, but it must be emphasised that the conclusions reached in this way represent strong probabilities rather than certainties, and that only binary mixtures have been considered.

The results of the hydrolysis experiments for the various phenoxy-chlorides, $(PhO)_nPCl_{5-n}$, are collected in Table 1; in this and the other similar Tables the molecular weight is that read off from the curve relating the molecular weight of the dimeric compounds to the halogen content.

The three specimens (preparations 1, 2, and 3) of the tetraphenoxy-monochloride are clearly all the same; recrystallisation led to no change in chlorine content and there is every indication that they are three specimens of a single compound. The results of hydrolysis agree well with those calculated for $[(PhO)_4P]^+[(PhO)_4PCl_2]^-$ or the hydrolytically indistinguishable $[(PhO)_3PCl]^+[(PhO)_5PCl]^-$, $[(PhO)_4P]^+Cl^-$, or $[(PhO)_3PCl]^+[PhO]^-$; the last structure may be ruled out as highly improbable but further evidence is needed to distinguish between the other three. It is noteworthy that this compound is apparently present in the mixture (preparation 6) obtained by treating triphenyl phosphite with chlorine (1 mol.) in the absence of diluent.

The marked difference between the two random samples (preparations 4 and 5) of the crude triphenoxy-dichloride from triphenyl phosphite and chlorine without diluent clearly show this to be a mixture; the hydrolysis figures for the bulk sample (preparation 6) are in best agreement with either a mixture of $[(PhO_4)P]^+[(PhO)_3PCl_3]^-$ {or its hydrolytic equivalent $[(PhO)_3PCl]^+[(PhO)_4PCl_2]^-$} and $[(PhO)_4P]^+[PhO{\cdot}PCl_5]^-$ {or its hydrolytic equivalent $[PhO{\cdot}PCl_3]^+[(PhO)_4PCl_2]^-$} in the molar ratio 47 : 53, or a mixture of $[(PhO)_4P]^+[(PhO)_4PCl_2]^-$ {or its equivalents $[(PhO)_3PCl]^+[(PhO)_5PCl]^-$, $[(PhO)_4P]^+Cl^-$, and $[(PhO)_3PCl]^+[OPh]^-$} and $[(PhO)_3PCl]^+[PhO{\cdot}PCl_5]^-$ {or $[PhO{\cdot}PCl_3]^+[(PhO)_3PCl_3]^-$} in the molar ratio 48 : 52. The figures for preparation 4 agree fairly well with the latter mixture in the modified molar ratio 58 : 42, but those for preparation 5 do not agree satisfactorily with those calculated for any binary mixture.

The dichloride prepared in *n*-hexane appears to be less heterogeneous, the mean figures for the two samples (preparations 7 and 8) agreeing quite well with those calculated for a mixture of either $[(PhO)_4P]^+[(PhO)_2PCl_4]^-$ or $[(PhO)_2PCl_2]^+[(PhO)_4PCl_2]^-$ and $[(PhO)_3PCl]^+[(PhO)_3PCl_3]^-$ or $[(PhO)_3PCl]^+Cl^-$ in the molar ratio 2 : 1. Precipitation of this material from ethylene dichloride with ether (preparation 9) or equilibration in acetonitrile (preparations 10 and 11) gives very similar products which differ little from the material (preparation 12) prepared from triphenyl phosphite and chlorine in acetonitrile; the mean hydrolysis figures for these four products are in good agreement with those calculated for an equimolecular mixture of $[(PhO)_4P]^+[(PhO)_4PCl_2]^-$ {or the equivalents $[(PhO)_3PCl]^+[(PhO)_5PCl]^-$, $[(PhO)P_4]^+Cl^-$, and $[(PhO)_3PCl]^+[OPh]^-$} and $[(PhO)_3PCl]^+[PhO{\cdot}PCl_5]^-$ {or $[PhO{\cdot}PCl_3]^+[(PhO)_3PCl_3]^-$} or a similar mixture of $[(PhO)_3PCl]^+[(PhO)_3PCl_3]^-$ {or $[(PhO)_3PCl]^+Cl^-$} and $[PhO{\cdot}PCl_3]^+[(PhO)_5PCl]^-$. The figures for the phenoxy-chloride prepared from phosphorus pentachloride and 3 mols. of phenol (preparations 13 and 14) show this to be a complex mixture.

TABLE 1. *Hydrolysis products of phenoxy-chlorides,* $(PhO)_nPHal_{5-n}$.

Method of prepn.	Prep. no.	Cl (%)	*M*	Hydrolysis products (mol.) Cl^-	$(PhO)_3PO$	PhOH	H^+
$2(PhO)_3P + Cl_2$ in PhCl :							
Crude product	1	8·4	875	2·06	1·96	1·98	2·00
Recryst. from $C_2H_4Cl_2$–PhCl	2	8·2	878	2·03	1·97	1·98	2·00
$4PhOH + PCl_5$:							
Crude product	3	8·2	878	2·03	1·96	1·96	2·00
$(PhO)_3P + Cl_2$ without diluent :							
Random sample 1	4	16:7	778	3·66	1·56	1·20	4·18
Random sample 2	5	26·9	690	5·27	1·34	0·77	6·54
Bulk sample	6	18·8	758	4·06	1·41	0·90	4·55
$(PhO)_3P + Cl_2$ in *n*-hexane :							
Sample 1	7	18·9	757	4·07	1·27	0·73	4·62
Sample 2	8	18·7	759	4·05	1·34	0·67	4·66
Pptd. from $C_2H_4Cl_2$ with Et_2O	9	18·9	757	4·07	1·54	1·01	4·42
Kept in MeCN for 10 min.	10	18·8	758	4·06	1·50	1·07	4·45
Kept in MeCN for 24 hr.	11	18·7	759	4·05	1·51	1·01	4·49
$(PhO)_3P + Cl_2$ in MeCN :							
Pptd. with Et_2O	12	18·3	764	3·97	1·50	1·00	4·47
$3PhOH + PCl_5$:							
Pptd. from $C_2H_4Cl_2$ with Et_2O	13	20·7	743	4·32	1·46	0·99	4·78
Recryst. from PhCl	14	16·8	777	3·69	1·58	1·21	4·08
$(PhO)_2PCl + Cl_2$ without diluent :							
Crude product	15	31·6	655	5·85	0·97	0·72	7·02
$(PhO)_2PCl + Cl_2$ in *n*-hexane :							
Recryst. from PhCl	16	32·6	646	6·00	1·01	0·68	6·97
Pptd. from PhCl with Et_2O	17	32·8	649	6·03	0·98	0·67	6·97
$(PhO)_2PCl + Cl_2$ in MeCN :							
Pptd. with Et_2O	18	32·7	647	6·01	1·02	0·70	7·02
$2PhOH + PCl_5$:							
Recryst. from $C_2H_4Cl_2$	19	32·8	649	6·03	1·00	0·68	6·99
$PhOH + PCl_5$:							
Crude product	20	53·9	526	8·04	0·47	0·00	9·52
Pptd. from $C_2H_4Cl_2$ with Et_2O	21	53·6	530	8·00	0·48	0·00	9·54
Recryst. from $C_2H_4Cl_2$	22	53·7	529	8·01	0·50	0·00	9·46

Apart from the preparation (No. 15) from diphenyl phosphorochloridite and chlorine without diluent, which is slightly deficient in chlorine, all the preparations (Nos. 16, 17, 18, and 19) of the diphenoxy-dichloride are closely similar. Results of hydrolysis, however, show clearly that they are mixtures, agreeing excellently with those calculated for a mixture of $[(PhO)_4P]^+[PCl_6]^-$ {or $[PCl_4]^+[(PhO)_4PCl_2]^-$ and $[(PhO)_3PCl]^+[PhO{\cdot}PCl_5]^-$ {or $[PhO{\cdot}PCl_3]^+[(PhO)_3PCl_3]^-$} in the molar ratio 2 : 1.

The three specimens of the phenoxy-tetrachloride (preparations 20, 21, and 22) are again closely similar. These, too, are mixtures, results of hydrolysis agreeing excellently with those calculated for an equimolecular mixture of $[(PhO)_3PCl]^+[PCl_6]^-$ {or $[PCl_4]^+[(PhO)_3PCl_3]^-$} and $[PhO{\cdot}PCl_3]^+[PCl_6]^-$ {or $[PCl_4]^+[PhO{\cdot}PCl_5]^-$}.

Among the preparations so far described only one pure compound, *viz.*, $[(PhO)_4P]^+[(PhO)_4PCl_2]^-$ (or its equivalents), has been encountered. All the other preparations are mixtures, and microscopic examination, especially in polarised light, shows the presence in them of more than one type of crystal. Limited success has attended attempts to isolate pure compounds by hand-sorting and by fractional crystallisation.

By such procedures, pure specimens of $[(PhO)_4P]^+[(PhO)_3PCl_3]^-$ {or the hydrolytically indistinguishable $[(PhO)_3PCl]^+[(PhO)_4PCl_2]^-$}, one of the probable components of the crude triphenoxy-dichloride prepared from triphenyl phosphite and chlorine, and of

$[(PhO)_4P]^+[PCl_6]^-$ {or the hydrolytically indistinguishable $[PCl_4]^+[(PhO)_4PCl_2]^-$}, one of the compounds probably present in the diphenoxy-trichloride prepared from diphenyl phosphorochloridite and chlorine, have been obtained from crude triphenoxy-dichloride prepared from phenol and phosphorus pentachloride. The compound $[(PhO)_4P]^+[PhO{\cdot}PCl_5]^-$ {or the hydrolytically indistinguishable $[PhO{\cdot}PCl_3]^+[(PhO)_4PCl_2]^-$}, another probable component of the crude triphenoxy-dichloride from triphenyl phosphite and chlorine, has been obtained similarly from crude diphenoxy-trichloride.

Data on the hydrolysis of the colourless tetraphenoxy-bromide and the yellow triphenoxy-dibromide are collected in Table 2. The three monobromide preparations (Nos. 23, 24, and 25) are clearly identical; the hydrolysis results indicate that they are all specimens of the single compound $[(PhO)_4P]^+[(PhO)_4PBr_2]^-$ {or the hydrolytically indistinguishable $[(PhO)_3PBr]^+[(PhO)_5PBr]^-$, $[(PhO)_4P]^+Br^-$, or $[(PhO)_3PBr]^+[OPh]^-$}, which is a component of the triphenoxy-dibromide. The dibromide shows some tendency to react further with bromine to form orange perbromides and to lose bromine on warming or exposure to high vacuum. Both preparations (Nos. 26 and 27) of the dibromide are clearly the same; results of hydrolysis agree well with those calculated for a mixture of $[(PhO)_4P]^+[(PhO)_4PBr_2]^-$ {or $[(PhO)_3PBr]^+[(PhO)_5PBr]^-$ or $[(PhO)_4P]^+Br^-$} and $[(PhO)_3PBr]^+[PBr_5]^-$ {or $[PhO{\cdot}PBr_3]^+[(PhO)_3PBr_3]^-$} in the molar ratio 52 : 48; this mixture is similar to one of those suggested for the crude triphenoxy-dichloride.

TABLE 2. *Hydrolysis products of phenoxy-bromides,* $(PhO)_nPBr_{5-n}$.

Method of prepn.	Prep. no.	Br (%)	*M*	Hydrolysis products (moles/mole) Br^-	$(PhO)_3PO$	PhOH	H^+
$2(PhO)_3P + Br_2$ in PhCl:							
Crude product	23	16·4	966	1·96	1·98	2·00	2·00
Recryst. from $C_2H_4Br_2$	24	16·5	966	1·97	1·98	1·99	2·00
Fractl. crystn. of 26 from PhCl	25	16·9	965	1·99	1·96	1·96	2·00
$(PhO)_3P + Br_2$ without diluent:							
Crude product	26	33·4	942	3·90	1·57	1·12	4·45
$(PhO)_3P + Br_2$ in MeCN:							
Pptd. with Et_2O	27	33·2	943	3·89	1·47	1·08	4·42

The reaction between triphenyl phosphite and iodine follows a rather different course from that with the other two halogens. At low temperatures the normal first stage [as equation (i)] is followed by a normal second stage:

$$[(PhO)_4P]^+I^- + (PhO)_2PI + I_2 \longrightarrow 2[(PhO)_3PI]^+I^-$$

but as the temperature is raised this is replaced by the alternative:

$$[(PhO)_4P]^+I^- + (PhO)_2PI + I_2 \longrightarrow [(PhO)_3PI]^+I_3^- + (PhO)_3P$$

which is the sole reaction at 60°. The periodide, $[(PhO)_3PI]^+I_3^-$, is also formed[7] by the action of iodine on the di-iodide, $[(PhO)_3PI]^+I^-$. All three products, *viz.*, tetraphenoxyphosphonium iodide, iodo(triphenoxy)phosphonium iodide and iodo(triphenoxy)phosphonium tri-iodide,[7] have been isolated in the pure state and their structures have been confirmed by the usual hydrolytic procedure. For steric reasons dimeric structures of the $[PX_4]^+[PY_6]^-$ type have not been considered in the iodine series; this view is supported by the preliminary results of an *X*-ray crystallographic investigation of the periodide now in progress in these laboratories.[8]

The choice between the monomeric, $[PX_4]^+Y^-$, and dimeric, $[PX_4]^+[PY_6]^-$, structures is not quite so obvious for the chlorides and bromides. The classical work of Clark, Powell, and Wells[9] showed crystalline phosphorus pentachloride to be the dimer, $[PCl_4]^+[PCl_6]^-$, and Payne[10] has shown that this form is also present in the electrically conducting solutions of phosphorus pentachloride in several solvents. Crystalline phosphorus pentabromide,

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[7] Forsman and Lipkin, *J. Amer. Chem. Soc.*, 1953, **75**, 3145.

[8] Bartindale and Farrow, personal communication.

[9] Clark, Powell, and Wells, *J.*, 1942, 642.

[10] Payne, *J.*, 1953, 1052.

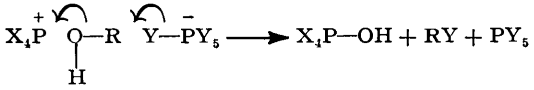
however, has been shown[11] to be the monomer, $[PBr_4]^+Br^-$, while the nature of the ions present in its conducting solutions is undecided.* There can be no reasonable doubt that the various phenoxy-chlorides should be assigned dimeric structures, $[(PhO)_xPCl_{4-x}]^+[(PhO)_yPCl_{6-y}]^-$, since, not only do the large majority of the hydrolysis results fail to give satisfactory agreement with those calculated for binary mixtures of monomers of the type $[PX_4]^+Y^-$, but two of the four pure compounds of this series isolated in the course of the present work, *viz.*, $[(PhO)_4P]^+[(PhO)_3PCl_3]^-$ and $[(PhO)_4P]^+[PhO{\cdot}PCl_5]^-$ are stoicheiometrically incapable of formulation as monomers. The latter type of stoicheiometric evidence is not available for the phenoxy-bromides, but failure to obtain satisfactory agreement between the observed hydrolysis results for the triphenoxy-dibromide and those calculated for mixtures of monomers leads us to conclude that the phenoxy-bromides likewise have dimeric structures of the general formula, $[(PhO)_xPBr_{4-x}]^+[(PhO)_yPBr_{6-y}]^-$.

The hydrolytic experiments so far described do not always lead to unambiguous conclusions regarding structure, since, as has already been pointed out, several isomeric structures may behave identically on hydrolysis. Certain of these ambiguities may be resolved on the basis of alcoholysis experiments. For this purpose, the halide under investigation was equilibrated in anhydrous acetonitrile and then treated with 2 mols. of propan-1-ol.† When reaction was complete, an excess of water was added, and the product analysed by the same procedure as was used in the simple hydrolysis experiments; the amount of alkyl halide produced was estimated by difference. The results of these experiments are summarised in Table 3.

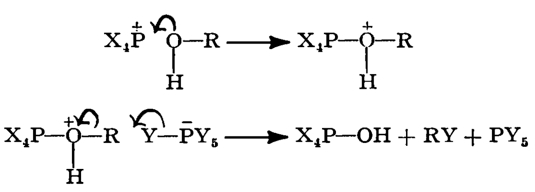
TABLE 3. *Alcoholysis of phenoxy-halides,* $(PhO)_nPHal_{5-n}$.

	Products (moles/mole)				
Empirical formula of halide	Hal^-	$(PhO)_3PO$	PhOH	H^+	RHal
$(PhO)_4PCl$	0·00	1·98	1·97	0·00	2·00
$(PhO)_3PCl_2$	2·12	1·52	1·06	2·46	1·88
$(PhO)_2PCl_3$	4·20	1·04	0·66	5·24	1·80
$PhO{\cdot}PCl_4$	5·76	0·44	0·00	7·24	2·24
$(PhO)_4PBr$	0·00	1·97	1·97	0·00	2·00
$(PhO)_3PBr_2$	1·92	1·49	1·08	2·35	2·08

The mechanism previously advanced[3,6] for the action of the phenoxy-halides on alcohols requires modification in the light of the dimeric ionic structures now established for these compounds. Reaction of compounds of the general type $[PX_4]^+[PY_6]^-$ with an alcohol is most reasonably regarded as involving attack on the oxygen atom of the alcohol by the cation, and attack on the alkyl group of the alcohol by one of the nucleophilic halogen atoms of the anion; these processes may be simultaneous :



or successive :



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* Since this work was completed, Dr. D. S. Payne has informed us that unpublished work with Mr. G. S. Harris shows that, in acetonitrile, phosphorus pentabromide ionises largely as $[PBr_4]^+[PBr_6]^-$; we are much indebted to Dr. Payne for his courtesy in making this information available to us in advance of publication.

† Less satisfactory results were obtained with methanol, possibly owing to the difficulty of ensuring the absence of all traces of water, and with butan-1-ol, owing to interference with the analytical procedure.

[11] Powell and Clark, *Nature*, 1940, **145**, 971; van Driel and MacGillavry, *Rec. Trav. chim.*, 1943, **62**, 167.

but in either event the optical inversion observed[3,6] with optically active secondary alcohols is accounted for. The process will be completed by loss of HX from the hydroxylated cation :

$$\mathrm{X_4P\text{-}OH \longrightarrow X_3P{=}O + HX}$$

This general mechanism, which may be regarded as an extension of both our earlier mechanism and Gerrard's " end-on " mechanism[12] for the action of phosphorus pentachloride on alcohols, has been used in formulating the reaction of the first mol. of alcohol in the alcoholysis experiments; the reaction of the second mol. and of the water has been assumed to involve normal hydrolysis of $X_3P{=}O$ and PY_5, with the exception that one mol. of hydrogen halide is replaced by one of alkyl halide if either $X_3P{=}O$ or PY_5 contains the necessary halogen atom.

For the tetraphenoxy-monochloride and -monobromide, two dimeric structures are possible (cf. pp. 3046 and 3048). The expected alcoholysis products are thus either those resulting from the reactions :

$$\mathrm{[(PhO)_4P]^+[(PhO)_4PHal_2]^- + ROH \longrightarrow (PhO)_3PO + PhOH + RHal + (PhO)_4PHal}$$
$$\mathrm{(PhO)_4PHal + ROH \longrightarrow RHal + (PhO)_3PO + PhOH}$$

i.e., the overall reaction

$$\mathrm{[(PhO)_4P]^+[(PhO)_4PHal_2]^- + 2ROH \longrightarrow 2(PhO)_3PO + 2PhOH + 2RHal}$$

or those resulting from the alternative reactions :

$$\mathrm{[(PhO)_3PHal]^+[(PhO)_5PHal]^- + ROH \longrightarrow (PhO)_3PO + HHal + RHal + (PhO)_5P}$$
$$\mathrm{(PhO)_5P + H_2O \longrightarrow (PhO)_3PO + 2PhOH}$$

i.e., the overall reaction

$$\mathrm{[(PhO)_3PHal]^+[(PhO)_5PHal]^- + ROH + H_2O \longrightarrow HHal + 2(PhO)_3PO + 2PhOH + RHal}$$

Reference to Table 3 shows that only the first alternative agrees with the experimental findings. We therefore conclude that both tetraphenoxy-monohalides are the tetraphenoxyphosphonium tetraphenoxydihalogenophosphates, $[(PhO)_4P]^+[(PhO)_4PHal_2]^-$.

The alcoholysis results eliminate only one of the possible components of the mixtures which may, on the basis of the hydrolysis experiments, make up the acetonitrile-equilibrated triphenoxy-dichloride. The expected products from the possible components of one of these mixtures are those of the reactions :

$$\mathrm{[(PhO)_4P]^+[(PhO)_4PCl_2]^- + 2ROH \longrightarrow 2(PhO)_3PO + 2PhOH + 2RCl}$$
$$\mathrm{[(PhO)_3PCl]^+[(PhO)_5PCl]^- + ROH + H_2O \longrightarrow HCl + 2(PhO)_3PO + 2PhOH + RCl}$$
$$\left\{\begin{array}{c}\mathrm{[(PhO)_3PCl]^+[PhO{\cdot}PCl_5]^-} \\ \text{or} \\ \mathrm{[PhO{\cdot}PCl_3]^+[(PhO)_3PCl_3]^-}\end{array}\right\} \mathrm{+ ROH + H_2O \longrightarrow 4HCl + (PhO)_3PO + PhO{\cdot}PO(OH)_2 + 2RCl}$$

of which the first two are alternatives. Only an equimolecular combination of the first and the third reaction could lead to products [2 mols. Cl^-, 1·5 mols. $(PhO)_3PO$, 1 mol. PhOH, 2·5 mols. H^+, and 2 mols. RCl] in reasonable agreement with the experimental findings. The same mixture would result from equimolecular combination of the two reactions :

$$\mathrm{[(PhO)_3PCl]^+[(PhO)_3PCl_3]^- + 2ROH \longrightarrow 2HCl + 2(PhO)_3PO + 2RCl}$$
$$\mathrm{[PhO{\cdot}PCl_3]^+[(PhO)_5PCl]^- + 2ROH + 2H_2O \longrightarrow}$$
$$\mathrm{2HCl + (PhO)_3PO + 2PhOH + PhO{\cdot}PO(OH)_2 + 2RCl}$$

which correspond to the components of the alternative possible mixtures.

In the cases of the tri- and tetra-chlorides, the alcoholysis results confirm the conclusions

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[12] Gerrard, *J.*, 1946, 741.

drawn from the hydrolysis experiments but throw no further light on the structures of the components of the mixtures involved. For the trichloride the relevant equations are :

$$\left\{\begin{matrix}[(PhO)_4P]^+[PCl_6]^- \\ \text{or} \\ [PCl_4]^+[(PhO)_4PCl_2]^-\end{matrix}\right\} + 2ROH + 3H_2O \longrightarrow 4HCl + (PhO)_3PO + PhOH + H_3PO_4 + 2RCl$$

$$\left\{\begin{matrix}[(PhO)_3PCl]^+[PhO{\cdot}PCl_5]^- \\ \text{or} \\ [PhO{\cdot}PCl_3]^+[(PhO)_3PCl_3]^-\end{matrix}\right\} + 2ROH + 2H_2O \longrightarrow 4HCl + (PhO)_3PO + PhO{\cdot}PO(OH)_2 + 2RCl$$

A 2 : 1 mixture would be expected to give 4 mols. of chloride ion, 1 mol. of triphenyl phosphate, 0·67 mol. of phenol, 5 mols. of acid, and 2 mols. of alkyl chloride, in reasonable agreement with the experimental findings. Similarly, the equations for the tetrachloride are :

$$\left\{\begin{matrix}[(PhO)_3PCl]^+[PCl_6]^- \\ \text{or} \\ [PCl_4]^+[(PhO)_3PCl_3]^-\end{matrix}\right\} + 2ROH + 3H_2O \longrightarrow 5HCl + (PhO)_3PO + H_3PO_4 + 2RCl$$

$$\left\{\begin{matrix}[PhO{\cdot}PCl_3]^+[PCl_6]^- \\ \text{or} \\ [PCl_4]^+[PhO{\cdot}PCl_5]^-\end{matrix}\right\} + 2ROH + 5H_2O \longrightarrow 7HCl + PhO{\cdot}PO(OH)_2 + H_3PO_4 + 2RCl$$

leading to products [6 mols. Cl^-, 0·5 mol. $(PhO)_3PO$, 7·5 mols. H^+, and 2 mols. RCl] in reasonable agreement with those found experimentally.

The alcoholysis experiments with the dibromide allow of a partial discrimination between the possibilities emerging from the hydrolysis experiments. The case is the same as that of the first possible mixture for the dichloride and the same reasoning leads to the elimination of $[(PhO)_3PBr]^+[(PhO)_5PBr]^-$ as a possible component.

TABLE 4. *Structures and compositions of phenoxyphosphorus halides.*

(a) *Pure compounds.*

Empirical formula	Prep. no.	Structure	Name
$(PhO)_4PCl$	1, 2, 3	$[(PhO)_4P]^+[(PhO)_4PCl_2]^-$	Tetraphenoxyphosphonium tetraphenoxydichlorophosphate
$(PhO)_{3\frac{1}{2}}PCl_{1\frac{1}{2}}$	—	$[(PhO)_4P]^+[(PhO)_3PCl_3]^-$ *	Tetraphenoxyphosphonium triphenoxytrichlorophosphate
$(PhO)_{2\frac{1}{2}}PCl_{2\frac{1}{2}}$	—	$[(PhO)_4P]^+[PhO{\cdot}PCl_5]^-$ *	Tetraphenoxyphosphonium phenoxypentachlorophosphate
$(PhO)_2PCl_3$	—	$[(PbO)_4P]^+[PCl_6]^-$ *	Tetraphenoxyphosphonium hexachlorophosphate
$(PhO)_4PBr$	23, 24 25	$[(PhO)_4P]^+[PhO)_4PBr_2]^-$	Tetraphenoxyphosphonium tetraphenoxydibromophosphate
$(PhO)_4PI$	—	$[(PhO)_4P]^+I^-$	Tetraphenoxyphosphonium iodide
$(PhO)_3PI_2$	—	$[(PhO)_3PI]^+I^-$	Iodotriphenoxyphosphonium iodide
$(PhO)_3PI_4$	—	$[(PhO)_3PI]^+I_3^-$	Iodotriphenoxyphosphonium tri-iodide

(b) *Mixtures.*

Empirical formula	Prep. no.	Components *	Molar ratio
$(PhO)_3PCl_2$	6	$[(PhO)_4P]^+[(PhO)_3PCl_3]^-$; $[(PhO)_4P]^+[PhO{\cdot}PCl_5]^-$; $[(PhO)_4P]^+[(PhO)_4PCl_2]^-$; $[(PhO)_3PCl]^+[PhO{\cdot}PCl_5]^-$	1 : 1 : 1 : 1
,, ...	7, 8	$[(PhO)_4P]^+[(PhO)_2PCl_4]^-$; $[(PhO)_3PCl]^+[(PhO)_3PCl_3]^-$	2 : 1
,, ...	9, 10, 11, 12	$[(PhO)_4P]^+[(PhO)_4PCl_2]^-$; $[(PhO)_3PCl]^+[PhO{\cdot}PCl_5]^-$	1 : 1
$(PhO)_2PCl_3$	16, 17, 18, 19	$[(PhO)_4P]^+[PCl_6]^-$; $[(PhO)_3PCl]^+[PhO{\cdot}PCl_5]^-$	2 : 1
$PhO{\cdot}PCl_4$	20, 21, 22	$[(PhO)_3P]^+[PCl_6]^-$; $[PhO{\cdot}PCl_3]^+[PCl_6]^-$	1 : 1
$(PhO)_3PBr_2$	26, 27	$[(PhO)_4P]^+[(PhO)_4PBr_2]^-$; $[PhO{\cdot}PBr_3]^+[(PhO)_3PBr_3]^-$	1 : 1

* Probable.

Our conclusions regarding the structures and compositions of the various products obtained in the course of our work are collected in Table 4. Conclusions shown without comment are those which follow unequivocally from the experimental results. Those shown as " probable " are our choice between the alternatives which remain after all the experimental facts have been taken into consideration; in making this choice for the chlorides we have always preferrred structures in which there is a preponderance of chlorine in the anion, since this seems to us a reasonable basis for discrimination. In the case of the triphenoxy-dibromide, however, we have rejected the structure $[(PhO)_3PBr]^+[PhO{\cdot}PBr_5]^-$ on the basis of the relative stereochemical difficulty of accommodating five bromine atoms in the anion.

We have also prepared tri-2 : 6-xylyloxy-dihalides from tri-2 : 6-xylyl phosphite and chlorine, bromine, and iodine. Although these have not been fully investigated the high yield of tri-2 : 6-xylyl phosphate obtained on hydrolysis indicates that the dichloride is chlorotri-2 : 6-xylyloxyphosphonium tri-2 : 6-xylyloxytrichlorophosphate, $[(Me_2C_6H_3{\cdot}O)_3PCl]^-[(Me_2C_6H_3{\cdot}O)_3PCl_3]^-$; the di-iodide is almost certainly iodotri-2 : 6-xylyloxyphosphonium iodide, $[(Me_2C_6H_3{\cdot}O)_3PI]^+I^-$, but the nature of the dibromide is uncertain.

EXPERIMENTAL

Rigid exclusion of moisture is essential in handling the various aryloxy-halides and manipulations were carried out in a dry-box; all solvents were rigorously dried before use. M. p.s are of little diagnostic value and were not generally determined; in cases where they were, the procedure was to transfer the finely powdered halide, under light petroleum (b. p. 40—60°) in a closed system, to a capillary tube; the light petroleum was then removed under reduced pressure, and the tube sealed before the m. p. was determined in the usual manner.

For the hydrolyses, the halide (*ca.* 500 mg.) was weighed in a dry, tared flask; water (50 ml.) was then added by means of a stoppered funnel, the whole system being closed. After being kept, with occasional shaking, for a minimum of 4 hr., the precipitated triphenyl phosphate was collected quantitatively on a sintered-glass crucible, washed with water, and dried to constant weight (over P_2O_5) *in vacuo* at room temperature. The filtrate and washings were made up with water to 500 ml. Aliquot parts of this solution were then taken for the determination of halide ion, gravimetrically as silver halide, hydrogen ion, by titration to pH 3—5 either by use of screened Congo-red or potentiometrically, and phenol, colorimetrically by the method of Folin and Ciocalteu.[13]

For the alcoholyses, the halide, weighed in a dry flask as before, was treated with sufficient dry acetonitrile to effect solution and left for 4 hr. at room temperature. A 20% solution of propan-1-ol (2 mols.) in dry acetonitrile was then added at *ca.* −10°, and the reaction allowed to proceed at room temperature for 1 hr. Water (50 ml.) was then added, and the same procedure followed as in the hydrolysis experiments.

Phenoxy-chlorides, $(PhO)_nPCl_{5-n}$.

Tetraphenoxy-chloride, $(PhO)_4PCl$.—(*a*) Chlorine (7·1 g., 0·1 mole) was passed into a stirred solution of triphenyl phosphite (62 g., 0·2 mole) in chlorobenzene (25 ml.) cooled in an ice–salt bath. A white solid separated during the reaction and was finally completely precipitated by addition of dry ether (750 ml.); recrystallisation of this product (preparation 1) from chlorobenzene–ethylene dichloride (1 : 1) afforded *tetraphenoxyphosphonium tetraphenoxydichlorophosphate* (preparation 2) as plates (Found: Cl, 8·2. $C_{48}H_{40}O_8Cl_2P_2$ requires Cl, 8·1%); hydrolysis results are recorded in Table 1 and alcoholysis results in Table 3.

Evaporation of the original filtrate and distillation of the residue yielded diphenyl phosphorochloridite (20·5 g., 82%), b. p. 170—173°/11 mm., n_D^{20} 1·5602 (Noack [1] gives b. p. 172°/11 mm.). This ester, in dry ether, was treated with aniline (2 mols.), also in dry ether; filtration from precipitated aniline hydrochloride, evaporation, and two recrystallisations from benzene afforded *diphenyl* N-*phenylphosphoramidite* (80% yield), m. p. 56—57° not depressed on admixture with a specimen prepared similarly from authentic diphenyl phosphorochloridite (Found: N, 4·4. $C_{18}H_{16}O_2NP$ requires N, 4·5%).

Butan-1-ol (7·4 g., 0·1 mole) was added slowly to the tetraphenoxy-chloride (43·8 g., 0·05 mole) with stirring and cooling. After an hour, *n*-butyl chloride was distilled under reduced pressure into a trap at −60°; solution of the distillate in ether, followed by washing, drying, and distillation of the extract, afforded butyl chloride (8·44 g., 91%), b. p. 76—80°, n_D^{20}

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[13] Folin and Ciocalteu, *J. Biol. Chem.*, 1927, **73**, 627.

1·4015. The residue from the initial distillation was shaken with 2N-sodium hydroxide (100 ml.); the insoluble triphenyl phosphate (30·7 g., 99%) was filtered off and washed with water; acidification of the filtrate afforded phenol, which was converted into 2 : 4 : 6-tribromophenol (32·6 g., 98·5%), m. p. 91—94°.

(*b*) Phenol (37·6 g., 0·4 mole) and phosphorus pentachloride (20·8 g., 0·1 mole) were heated together at 120° for 4 hr. The cooled product was washed with ether until it solidified and then pumped out at 20 mm. for 4 hr. to remove ether and hydrogen chloride. Analytical data for this preparation (No. 3) are recorded in Table 1.

Triphenoxy-dichlorides, $(PhO)_3PCl_2$.—(*a*) Chlorine (7·1 g., 0·1 mole) was passed slowly (30 min.), with stirring, into ice-cooled triphenyl phosphite (31 g.; 0·1 mole). The resulting, very pale green solid was broken up and kept at room temperature for 2 hr.; preparations 4 and 5 are random samples of this material. The bulk sample (preparation 6) was obtained by powdering the remainder of the product under dry ether and removing the ether by decantation and then under slightly reduced pressure at 40°. Analytical data for these preparations are recorded in Table 1.

A sample of the crude material (8 g.) was treated at room temperature with propan-1-ol (3 g.). The product was treated with an excess of 2N-sodium hydroxide and extracted with ether; evaporation of the washed and dried extract afforded triphenyl phosphate (4·9 g., 1·5 mol.), m. p. and mixed m. p. 46—48° after recrystallisation from aqueous ethanol. Acidification of the alkaline extract, followed by extraction with ether, afforded phenol (0·95 g., 1·0 mol.).

(*b*) Chlorine (7·1 g., 0·1 mole) was passed slowly into a well stirred, water-cooled solution of triphenyl phosphite (31 g., 0·1 mole) in *n*-hexane (250 ml.). The very pale green solid product was washed with several 250-ml. portions of ether and finally dried at room temperature under reduced pressure and powdered. Analytical data for two samples of this product (preparations 7 and 8) are given in Table 1, as also are those for the preparation (No. 9) obtained from it by addition of an excess of ether to a solution in the minimum of cold ethylene dichloride, and for solutions in the minimum of dry acetonitrile kept at room temperature for 10 min. (preparation 10) and 24 hr. (preparation 11). Alcoholysis data are in Table 3.

(*c*) Chlorine (7·1 g., 0·1 mole) was passed into a stirred mixture of triphenyl phosphite (31 g., 0·1 mole) and acetonitrile (15 ml.), cooled in ice–salt. After 10 min., ether (500 ml.) was added, and the precipitate washed with ether and dried under reduced pressure; analytical data for this preparation (No. 12) are given in Table 1.

(*d*) Phenol (28·2 g., 0·3 mole) was heated at 100° for 4 hr. with phosphorus pentachloride (20·9 g., 0·1 mole). The cooled product, which solidified after being washed thoroughly with ether, was dissolved in ethylene dichloride and precipitated by addition of ether; the last traces of hydrogen chloride were removed from this preparation (No. 13) at 15 mm. A portion of this material (10 g.) was dissolved in hot chlorobenzene (20 ml.). On slow cooling, the pale green solution deposited colourless crystals (*ca.* 3 g.) which were collected, washed with ether, and dried *in vacuo* (preparation 14). Analytical data for these preparations are given in Table 1.

Diphenoxy-trichlorides, $(PhO)_2PCl_3$.—(*a*) Chlorine (3·5 g., 0·05 mole) was passed slowly (30 min.) into stirred, cooled diphenyl phosphorochloridite[1] (12·6 g., 0·05 mole). The pale yellow solid was washed with ether and dried under reduced pressure. Analytical data for this preparation (No. 15) are given in Table 1.

(*b*) Chlorine (3·5 g., 0·05 mole) was passed slowly into a stirred, ice-cooled solution of diphenyl phosphorochloridite (12·6 g., 0·05 mole) in *n*-hexane (200 ml.). The solid product was washed well with ether, dried under reduced pressure, and dissolved in warm chlorobenzene. Preparation 16 is the crystalline solid which separated from this solution on slow cooling, while preparation 17 is the product precipitated from the mother-liquor by excess of ether; analytical data for both are in Table 1.

(*c*) Chlorine (3·5 g., 0·05 mole) was passed for 40 min. into a stirred solution of diphenyl phosphorochloridite (12·6 g.) in acetonitrile (10 ml.) at −10°. The product (preparation 18) was precipitated by adding ether (200 ml.), washed well with ether, and dried under reduced pressure; analytical data are given in Table 1.

(*d*) Phenol (37·6 g., 0·4 mole) and phosphorus pentachloride (41·8 g., 0·2 mole) were heated together at 110° for 4 hr. The product was washed with ether until it solidified and then recrystallised from hot ethylene dichloride, washed with ether, and dried *in vacuo*; analytical data for this preparation (No. 19) are given in Table 1.

Phenoxy-tetrachloride, $PhO{\cdot}PCl_4$.—Phenol (9·4 g., 0·1 mole) and phosphorus pentachloride (20·8 g., 0·1 mole) were heated together at 100° for 5 hr. The cooled solid product was washed with ether (4 × 250 ml.) and dried at 20 mm. Analytical data for this preparation (No. 20) are given in Table 1, as also are those for a preparation (No. 21) obtained by adding excess of ether to a solution in ethylene dichloride, and another (preparation 22) obtained by slow crystallisation from ethylene dichloride.

Pure Phenoxy-chlorides.—(a) *Tetraphenoxyphosphonium triphenoxytrichlorophosphate.* Crude triphenoxy-dichloride (preparation 13) (10 g.) was dissolved in the minimum of warm ethylene dichloride, and the solution set aside for 6 days. A large bipyramidal crystal (35 × 15 mm.), which separated from the solution, was removed, washed with ether, and dried *in vacuo* and proved to be the pure *salt* (Found: Cl, 13·4. $C_{42}H_{35}O_7Cl_3P_2$ requires Cl, 13·0%); the structure follows from the hydrolysis products {Found: Cl^-, 3·09; $(PhO)_3PO$, 1·93; PhOH, 0·99; H^+, 3·01. $[(PhO)_4P]^+[(PhO)_3PCl_3]^-$ requires Cl^-, 3·00; $(PhO)_3PO$, 2·00; PhOH, 1·00; H^+, 3·00 mols.}.

(b) *Tetraphenoxyphosphonium phenoxypentachlorophosphate.* Crude diphenoxy-trichloride (preparation 18) (10 g.) was dissolved in the minimum of ethylene dichloride and the solution set aside for 2 days. Numerous small rhombohedra could be clearly distinguished from the other crystals and were separated by hand under a dissecting microscope, washed with ether, and dried under reduced pressure. Analysis showed the *salt* (Found: Cl, 25·0. $C_{30}H_{25}O_5Cl_5P_2$ requires Cl, 25·2%) to have the structure assigned {Found on hydrolysis: Cl^-, 4·96; $(PhO)_3PO$, 1·01; PhOH, 0·99; H^+, 6·10. $[(PhO)_4P]^+[PhO{\cdot}PCl_5]^-$ requires Cl^-, 5·00; $(PhO)_3PO$, 1·00; PhOH, 1·00; H^+, 6·00 mols.}.

(c) *Tetraphenoxyphosphonium hexachlorophosphate.* Phosphorus pentachloride (20·8 g., 0·1 mole) and phenol (18·8 g., 0·2 mole) were heated together at 100° for 5 hr. The product was washed with ether, dried *in vacuo*, and dissolved in the minimum of ethylene dichloride–chlorobenzene (1 : 1). The supernatant liquid was decanted from the mass of small crystals which separated on cooling and carefully overlayered with ether. After two days a number of hexagonal plates were separated by hand from the other crystals and were washed with ether and dried *in vacuo*. The *salt* (Found: Cl, 31·9. $C_{24}H_{20}O_4Cl_6P_2$ requires Cl, 32·8%) was shown by hydrolysis to have the assigned structure {Found: Cl^-, 5·83; $(PhO)_3PO$, 1·00; PhOH, 0·95; H^+, 7·03. $[(PhO)_4P]^+[PCl_6]^-$ requires Cl^-, 6·00; $(PhO)_3PO$, 1·00; PhOH, 1·00; H^+, 7·00 mols.}.

Phenoxy-bromides, $(PhO)_nPBr_{5-n}$.

Tetraphenoxy-bromide, $(PhO)_4PBr$.—(*a*) Bromine (16 g., 0·1 mole), in chlorobenzene (25 ml.), was added slowly, with efficient stirring, to an ice-cold solution of triphenyl phosphite (62 g., 0·2 mole) in chlorobenzene (100 ml.). The deposited white solid was collected by filtration, washed with ether (4 × 200 ml.), and dried *in vacuo*. Recrystallisation of this product (preparation 23) from hot ethylene dibromide afforded pure *tetraphenoxyphosphonium tetraphenoxydibromophosphate* (preparation 24) (Found: Br, 16·5. $C_{48}H_{40}O_8Br_2P_2$ requires Br, 16·6%), the structure following from the nature of the hydrolysis products (Table 2). Alcoholysis data are in Table 3.

The original filtrate, worked up as described for the corresponding chloride, afforded diphenyl phosphorobromidite (20 g., 67·5%), b. p. 131—135°/0·15 mm., n_D^{20} 1·6003 (lit.[14] b. p. 189—192°/11 mm.), characterised by conversion into diphenyl *N*-phenylphosphoramidite (80% yield), m. p. and mixed m. p. 56—57° after recrystallisation from benzene.

(*b*) Crude triphenoxy-dibromide (preparation 26) was twice crystallised from hot chlorobenzene, and the product (preparation 25) washed with ether and dried *in vacuo*; for analytical data see Table 2.

Triphenoxy-dibromide, $(PhO)_3PBr_2$.—(*a*) Bromine (16·0 g., 0·1 mole) was added, with stirring, during 30 min. to water-cooled triphenyl phosphite (31 g., 0·1 mole); analytical data for the resulting solid (preparation 26) are recorded in Table 2.

(*b*) Bromine (8·0 g., 0·05 mole) was added, with stirring, during 1 hr. to a mixture of triphenyl phosphite (15·5 g.; 0·05 mole) and acetonitrile (10 ml.). Ether (250 ml.) was added, and the precipitated yellow solid washed with ether and dried under slightly reduced pressure at 0°; hydrolysis data for this preparation (No. 27) are given in Table 2 and alcoholysis data in Table 3.

Phenoxy-iodides, $(PhO)_nPI_{5-n}$.

Tetraphenoxyphosphonium Iodide.—(*a*) A solution of iodine (12·7 g.) in chloroform (100 ml.) was added slowly, with stirring, to triphenyl phosphite (31 g., 0·1 mole). When about 10% (0·005 mole) of the iodine had been added, the solution became yellow and the addition was

[14] Strecker and Grossmann, *Ber.*, 1916, **49**, 63.

stopped. Ether (500 ml.) was then added, and the precipitated *iodide* collected by filtration, washed with ether, and dried *in vacuo* (Found : I, 23·4. $C_{24}H_{20}O_4IP$ requires I, 23·5%); the structure is established by the nature of the hydrolysis products {Found : I^-, 0·99; $(PhO)_3PO$, 0·99; PhOH, 0·99; H^+, 1·00. $[(PhO)_4P]^+I^-$ requires I^-, 1·00; $(PhO)_3PO$, 1·00; PhOH, 1·00; H^+, 1·00 mol.}.

(*b*) The tetraphenoxy-chloride (preparation 12) (5 g.) was heated under reflux for 5 min. with methyl iodide (10 ml.) and ethylene dichloride (3 ml.). The resulting brown solution was allowed to cool to room temperature and then overlayered with ether. After 4 hr., the long, colourless, flat prisms of the iodide were collected, washed well with ether, and dried *in vacuo* [Found : I, 23·2. Hydrolysis products : I^-, 0·985; $(PhO)_3PO$, 0·995; PhOH, 0·955; H^+, 1·00 mol.].

Iodotriphenoxyphosphonium Iodide.—Iodine (25·4 g., 0·1 mole) was stirred at room temperature with triphenyl phosphite (31 g., 0·1 mole); the mixture solidified after 24 hr. and was then washed with light petroleum (b. p. 60—80°). Several recrystallisations from chlorobenzene at temperatures below 60° gave the *iodide* as small dark brown rhombs, m. p. 68—69° (Found : I, 46·2. $C_{18}H_{15}O_3I_2P$ requires I, 45·0%); the structure is established by the nature of the hydrolysis products {Found : I^-, 2·03; $(PhO)_3PO$, 0·92; PhOH, 0·00; H^+, 2·03. $[(PhO)_3PI]^+I^-$ requires I^-, 2·00; $(PhO)_3PO$, 1·00; PhOH, 0·00; H^+, 2·00 mols.}.

Iodotriphenoxyphosphonium Tri-iodide.—Recrystallisation of crude iodotriphenoxyphosphonium iodide (above) from hot chlorobenzene afforded the tri-iodide [7] as dark-red plates, m. p. 76—78° {Found : I, 62·2. Calc. for $C_{18}H_{15}O_3I_4P$: I, 62·2%. Hydrolysis products : I^-, 2·00; $(PhO)_3PO$, 0·98; PhOH, 0·00; H^+, 1·96; free I_2, 0·97. Calc. for $[(PhO)_3PI]^+I_3^-$: I^-, 2·00; $(PhO)_3PO$, 1·00; PhOH, 0·00; H^+, 2·00; I_2, 1·00 mol.}.

Halides from Tri-2 : 6-xylyl Phosphite.

Tri-2 : 6-xylyl Phosphite.—2 : 6-Xylenol (280 g., 1·9 mole) and phosphorus trichloride (89 g., 0·6 mole) were heated together on the steam-bath for 24 hr. Removal of hydrogen chloride and unchanged xylenol (40 g., b. p. 70—100°/1 mm.) left a solid which recrystallised from *n*-hexane, affording the *phosphite* (118 g., 50%), in rhombs, m. p. 83—84° (Found: C, 72·7; H, 6·8. $C_{24}H_{27}O_3P$ requires C, 73·1; H, 6·9%); a further 19 g. (8%) was obtained from the mother-liquor.

Chlorotri-2 : 6-xylyloxyphosphonium Tri-2 : 6-xylyloxytrichlorophosphate.—Chlorine (3·5 g., 0·05 mole) was passed slowly into a stirred solution of tri-2 : 6-xylyl phosphite (19·7 g., 0·05 mole) in light petroleum (b. p. 100—120°). The solid product was washed with ether (2 × 100 ml.) and recrystallised from warm chlorobenzene, affording the *salt* as needles, m. p. 124—125° (Found : Cl, 14·8. $C_{48}H_{54}O_6Cl_4P_2$ requires Cl, 15·25%). Hydrolysis of the salt (4·6 g.) with 2N-sodium hydroxide yielded *tri-2 : 6-xylyl phosphate* (4·0 g., 98%), m. p. 134—136°, raised to 137·5—138·5° by recrystallisation from light petroleum (b. p. 60—80°) (Found : C, 69·9; H, 6·8. $C_{24}H_{27}O_4P$ requires C, 70·2; H, 6·6%).

Iodotri-2 : 6-xylyloxyphosphonium Iodide.—Iodine (6·4 g., 0·025 mole) was added to tri-2 : 6-xylyl phosphite (10 g., 0·025 mole) in light petroleum (b. p. 60—80°) (100 ml.), and the mixture refluxed for 24 hr. The crystalline product was washed with light petroleum and ether and recrystallised from chlorobenzene, affording the *iodide*, probably contaminated with some tri-iodide, as black shining rhombs, m. p. 90—93° (Found : I, 42·1. $C_{24}H_{27}O_3I_2P$ requires I, 39·2%).

APPENDIX

Deduction of the Composition of Phenoxy-halides from their Hydrolysis Products.—The procedure used is illustrated below for the triphenoxy-dibromide (preparations 26 and 27).

Mean hydrolysis figures : Br^-, 3·90; $(PhO)_3PO$, 1·52; PhOH, 1·10; H^+, 4·44 moles/mole.

A table was constructed showing the calculated values for all binary mixtures of monomers or of dimers giving *ca.* 3·90 mols. of Br^- and for those binary mixtures of isomerides giving 4·00 mols. of Br^- which also give 1·52 mols. of $(PhO)_3PO$ or 1·10 mols. of PhOH. The following is a much abridged version of this table showing only the three best cases for the monomers and the six best cases for the dimers. All calculations are based on double molecules (*i.e.*, $[PX_4]^+[PY_6]^-$ or $2[PX_4]^+Y^-$). $\Sigma\Delta^2$ = sum of squares of differences between calculated and experimental values.

Entries 44*a* and 62*a* are those for Nos. 44 and 62 so adjusted as to minimise $\Sigma\Delta^2$; any adjustment of No. 33 increases $\Sigma\Delta^2$; no adjustment of Nos. 97, 98, and 99 can reduce $\Sigma\Delta^2$ below 100.

	Components		Molar	Hydrolysis products (mols.)				
No.	A	B	ratio	Br^-	$(PhO)_3PO$	PhOH	H^+	$10^4\Sigma\Delta^2$
12	$[I]^+Br^-$ or $[II]^+[OPh]^-$	$[IV]^+Br^-$	0·68 : 0·32	3·92	1·36	1·36	1·36	1080
14		$[V]^+Br^-$	0·76 : 0·24	3·92	1·52	1·52	4·40	1784
15	$[II]^+Br^-$	$[III]^+[OPh]^-$	0·75 : 0·25	4·00	1·50	0·50	4·50	3740
33	$[I]^+[XI]^-$ or $[II]^+[XII]^-$	$[II]^+[VII]^-$ or $[IV]^+[IX]^-$	0·42 : 0·58	3·90	1·42	1·26	4·48	372
44	$[I]^-[X]^-$ or $[II]^+[XI]^-$	$[II]^-[VII]^-$ or $[IV]^+[IX]^-$	0·52 : 0·48	3·92	1·52	1·04	4·40	56
62	$[I]^+[IX]^-$	$[I]^+[VII]^-$ or $[IV]^+[X]^-$	0·55 : 0·45	3·90	1·55	1·00	4·35	190
97	$[II]^+[IX]^-$	$[IV]^+[XI]^-$	0·52 : 0·48	4·00	1·52	0·96	4·48	312
98			0·45 : 0·55	4·00	1·45	1·10	4·55	270
99	$[II]^+[IX]^-$	$[V]^+[XII]^-$	0·52 : 0·48	4·00	1·52	0·96	4·48	312
44*a*	$[I]^+[X]^-$ or $[II]^+[XI]^-$	$[II]^+[VII]^-$ or $[IV]^+[IX]^-$	0·53 : 0·47	3·88	1·53	1·06	4·35	46
62*a*	$[I]^+[IX]^-$	$[I]^+[VII]^-$ or $[IV]^+[X]^-$	0·53 : 0·47	3·94	1·53	1·00	4·41	126

Clearly No. 44*a* is by far the best fit and it is therefore conluded that the dibromide is a mixture of $[(PhO)_4P]^+[(PhO)_4PBr_2]^-$ {or $[(PhO)_3PBr]^+[(PhO)_5PBr]^-$} and $[(PhO)_3PBr]^+[PhO{\cdot}PBr_5]^-$ {or $[PhO{\cdot}PBr_3]^+[(PhO)_3PBr_3]^-$} in the molar ratio 53 : 47.

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