

## Quasiphosphonium Intermediates. Part 3.<sup>1</sup> Preparation, Structure, and Reactivity of Alkoxyphosphonium Halides in the Reactions of Neopentyl Diphenylphosphinite, Dineopentyl Phenylphosphonite, and Trineopentyl Phosphite with Halogenomethanes and the Effect of Phenoxy-substituents on the Mechanism of Alkyl-Oxygen Fission in Michaelis-Arbuzov Reactions

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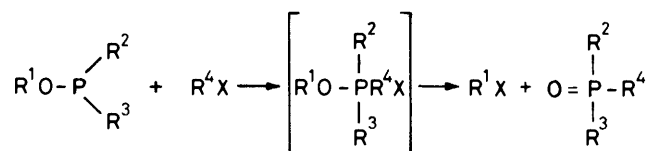
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The reactions of neopentyl diphenylphosphinite with chloro-, bromo-, or iodo-methane and of dineopentyl phenylphosphonite with bromo- or iodo-methane yield crystalline alkoxyphosphonium halides. In deuteriochloroform these intermediates decompose by a first-order process which involves rate-determining collapse of the phosphonium halide ion-pair with  $S_N2$ -type fission of the alkyl-oxygen bond. Rates for chloride, bromide, and iodide are similar. In a more ionising medium (deuterioacetonitrile) dissociation leads to stabilisation of the intermediates and to deviation from first-order decomposition. Previously determined X-ray diffraction data for the bromides, together with relative rates of decomposition in deuteriochloroform for intermediates in the series  $\text{Ph}_n(\text{RO})_{3-n}\text{P}^+\text{MeX}^-$  ( $n = 0, 1, \text{ or } 2$ ) suggest that the stability and reactivity of alkoxyphosphonium intermediates are determined largely by inductive rather than mesomeric effects of ligands. The presence of phenoxy-substituents on phosphorus may cause a tendency towards  $S_N1$ -type fission of the alkyl-oxygen bond in certain circumstances.

In the Michaelis-Arbuzov reaction of trialkyl phosphites with alkyl halides (Scheme 1;  $\text{R}^2 = \text{R}^3 = \text{R}^1\text{O}$ ) the first stage is usually rate determining.<sup>2</sup> Crystalline intermediates can nevertheless be isolated if the final dealkylation is retarded by steric hindrance ( $\text{R}^1 = \text{neopentyl}$ ).<sup>3,4</sup> Intermediates may also be obtained at 0 °C from the interactions of alkyl halides with alkyl dialkylphosphinites (Scheme 1;  $\text{R}^2 = \text{R}^3 = \text{alkyl}$ ),<sup>5-8</sup> dialkyl allylphosphonites (Scheme 1;  $\text{R}^2 = \text{R}^1\text{O}$ ,  $\text{R}^3 = \text{allyl}$  or 3-methylallyl),<sup>9-12</sup> or dialkyl alkylphosphonites (Scheme 1;  $\text{R}^2 = \text{R}^1\text{O}$ ,  $\text{R}^3 = \text{alkyl}$ ).<sup>13,14</sup> In these examples, the electron-releasing effect of the alkyl substituents on phosphorus increases the rate of the first stage of the reaction<sup>15</sup> and stabilizes the intermediate to some extent; neopentyl-derivatives, however, are the only types that can be stored at room temperature.<sup>9,10,14</sup>

The earlier uncertainty surrounding the structure of Michaelis-Arbuzov intermediates has largely been resolved by the use of <sup>31</sup>P n.m.r. spectroscopy which shows that the alkyl halide adducts have the tetraco-ordinate (phosphonium) structure in solution.<sup>3,4,13,16</sup> X-Ray crystal structure determinations on the methyl bromide adducts of dineopentyl phenylphosphonite and neopentyl diphenylphosphinite have also confirmed the phosphonium structure for these compounds in the solid state.<sup>17</sup> Although pentaco-ordinate intermediates have been identified by <sup>31</sup>P n.m.r. in the reactions of certain phosphites with halogens at low temperatures,<sup>18,19</sup> the possible role of such intermediates in the reactions of phosphorus(III) esters with alkyl halides is not clear. None has been detected spectroscopically and the stereochemical evidence for their involvement<sup>20,21</sup> appears to require further investigation.<sup>22</sup> In media such as benzene or chloroform the intermediates exist essentially as ion-pairs.<sup>4</sup>

Only a limited amount of information is available on the kinetics and mechanism of the product-forming stage of the Michaelis-Arbuzov reaction. The formation of alkyl halide with total or preponderant inversion of configuration<sup>23-26</sup> indicates nucleophilic attack by halide on the alkoxyphosphonium ion and it is likely that both  $S_N2$ - and  $S_N1$ -type mechanisms are involved according to the groups attached to phosphorus and the reaction conditions. In a number of



Scheme 1.

cases, neopentyl-oxo-phosphonium intermediates have been found to yield halides without rearrangement<sup>4,10,16,19,27-30</sup> in accord with the exclusive operation of the  $S_N2$  mechanism; but in other circumstances rearrangement may occur.<sup>16,19</sup> Rearrangement of secondary alkyl groups has also been observed in certain reactions.<sup>31</sup>

In order to obtain further information on the mechanisms by which Michaelis-Arbuzov intermediates decompose we have now prepared methyl halide adducts from dineopentyl phenylphosphonite and neopentyl diphenylphosphinite and have studied rates of decomposition in solution.<sup>16</sup> The effects of phenoxy-substituents on the mechanism of alkyl-oxygen fission in the Michaelis-Arbuzov reactions of dineopentyl phenyl phosphite and neopentyl diphenyl phosphite have also been investigated although intermediates could not be isolated in these cases.

### Results and Discussion

The preparations of methyltrineopentyl-oxo-phosphonium bromide and iodide have been described previously<sup>3,4</sup> and we now report the formation of similar adducts in the reactions of bromomethane or iodomethane with dineopentyl phenylphosphonite and neopentyl diphenylphosphinite at room temperature.<sup>16</sup> The reactions occurred more rapidly than with trineopentyl phosphite and were best carried out in anhydrous ether which served as a diluent and aided the precipitation of the phosphonium salts (Table 1). Neopentyl diphenylphosphinite was sufficiently reactive to yield an adduct with chloromethane but the corresponding chlorides could not be

**Table 1.** Preparations of quasiphosphonium halides from neopentyl diphenylphosphinite and from dineopentyl phenylphosphonite

Ester <sup>a</sup> (R = Me <sub>3</sub> CCH <sub>2</sub> )	Wt. (g)	Alkyl halide			Molecular formula	Isolated product: Ph <sub>2</sub> P(OR)R'X or PhP(OR) <sub>2</sub> R'X				Yield (%)	M.p. (°C)	
		R'X	Mol. equiv.	Time (days) <sup>b</sup>		Analysis (%)						
						C	H	X	P			
Ph <sub>2</sub> POR <sup>c</sup>	37.1	MeI	1.5	7	C <sub>18</sub> H <sub>24</sub> IOP	Found	52.0	5.9	30.6	8.1	91	130
						Requires	52.2	5.9	30.8	7.5		
Ph <sub>2</sub> POR <sup>d</sup>	3.3	MeBr	1.0	7	C <sub>18</sub> H <sub>24</sub> BrOP	Found	59.6	6.5	21.5	8.6	65	140
						Requires	58.7	6.6	21.7	8.5		
Ph <sub>2</sub> POR	5.4	MeCl	1.0	123	C <sub>18</sub> H <sub>24</sub> ClOP	Found	67.0	7.6	11.2	9.3	61	124
						Requires	67.0	7.5	11.0	9.6		
PhP(OR) <sub>2</sub> <sup>e</sup>	5.6	MeI	1.1	5	C <sub>17</sub> H <sub>30</sub> IO <sub>2</sub> P	Found	49.6	7.7	29.6	8.0	98	116
						Requires	48.2	7.1	30.0	7.3		
PhP(OR) <sub>2</sub> <sup>f</sup>	6.6	MeBr	1.1	7	C <sub>17</sub> H <sub>30</sub> BrO <sub>2</sub> P	Found	55.3	8.2	20.6	8.3	62	106
						Requires	54.0	8.0	21.2	8.2		

<sup>a</sup> In anhydrous ether if specified. <sup>b</sup> Reaction at room temperature. <sup>c</sup> In Et<sub>2</sub>O (140 ml). <sup>d</sup> In Et<sub>2</sub>O (10 ml). <sup>e</sup> In Et<sub>2</sub>O (30 ml). <sup>f</sup> In Et<sub>2</sub>O (10 ml).

**Table 2.** N.m.r. chemical shifts and coupling constants for quasiphosphonium halides and for their dealkylation products <sup>a</sup>

Compound (R = Me <sub>3</sub> CCH <sub>2</sub> )	<sup>31</sup> P δ (p.p.m.)	<sup>1</sup> H δ (p.p.m.)				Coupling constants (Hz)	
		Ph	CH <sub>2</sub> O	CH <sub>3</sub> P	Me <sub>3</sub> C	J <sub>POCH</sub>	J <sub>PCH</sub>
Ph <sub>2</sub> P(OR)MeI	+72 (m)	7.3—8.2 (m)	4.05 (d)	3.17 (d)	1.01 (s)	4.9	12.4
Ph <sub>2</sub> P(OR)MeBr	+72 (m)	7.3—8.2 (m)	4.05 (d)	3.26 (d)	1.02 (s)	4.9	13.0
Ph <sub>2</sub> P(OR)MeCl	+72 (m)	7.4—8.2 (m)	4.05 (d)	3.27 (d)	1.00 (s)	4.9	13.0
Ph <sub>2</sub> P(O)Me	+30 (q)	7.3—8.2 (m)		2.07 (d)	0.87 (s)		13.0
PhP(OR) <sub>2</sub> MeI	+74 (m) <sup>b</sup>	7.3—7.9 (m)	4.25 (d)	2.96 (d)	1.03 (s)	5.1	14.5
PhP(OR) <sub>2</sub> MeBr	+74 (m) <sup>b</sup>	7.3—8.0 (m)	4.27 (m)	3.06 (d)	1.03 (s)	5.1	14.0
PhP(O)(OR)Me	+41.5 (m)	7.3—8.0 (m)	3.51 (m)	1.67 (d)	0.91 (s)	5.3	14.5

<sup>a</sup> CDCl<sub>3</sub>. <sup>b</sup> Cf. δ +76 p.p.m. for PhP(OMe)<sub>2</sub>Me BF<sub>4</sub><sup>-</sup>. <sup>32</sup>

**Table 3.** Variation of <sup>31</sup>P chemical shift with structure for the quasiphosphonium halides (RO)<sub>n</sub>Ph<sub>3-n</sub><sup>+</sup>PMe X<sup>-</sup>

n	δ <sub>p</sub> (p.p.m.)	Ref.
3	+54 <sup>a</sup>	4
2	+74 <sup>a</sup>	b
1	+72 <sup>a</sup>	b
0	+22 <sup>c</sup>	33

<sup>a</sup> In CDCl<sub>3</sub>. <sup>b</sup> This work. <sup>c</sup> In CH<sub>2</sub>Cl<sub>2</sub>.

**Table 4.** <sup>31</sup>P chemical shift difference for quasiphosphonium halides (RO)<sub>n</sub>Ph<sub>3-n</sub><sup>+</sup>PMe X<sup>-</sup> and their dealkylation products (RO)<sub>n-1</sub>Ph<sub>3-n</sub>P(O)Me

n	δ <sub>p+OR</sub> - δ <sub>p=O</sub> (p.p.m.)
3	42.0
2	32.5
1	24.5

obtained from dineopentyl phenylphosphonite or trineopentyl phosphite. In these cases reaction was too slow and, on heating, only the Arbuzov products were obtained. Although anhydrous conditions are necessary for prolonged storage of the alkoxyphosphonium halides, they are surprisingly resistant to attack by atmospheric moisture and can be handled with ease in the open laboratory for the purpose of X-ray diffraction studies.<sup>17</sup> Unfortunately, the trineopentyl-oxo-derivatives have so far been obtained only as twinned crystals and structure determinations have not been possible.

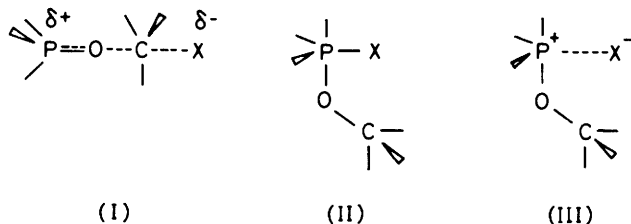
<sup>31</sup>P and <sup>1</sup>H n.m.r. data for the quasiphosphonium intermediates and for the corresponding Arbuzov products are given in Table 2. <sup>31</sup>P Chemical shifts for the intermediates are independent of the halogen present and are consistent with the phosphonium structure.<sup>32</sup> Replacement of alkoxy by phenyl in the series (RO)<sub>n</sub>Ph<sub>3-n</sub><sup>+</sup>PMe leads to a maximum downfield chemical shift of +74 p.p.m. for n = 2 (i.e. when one phenyl group is present), although the value moves upfield again as further phenyl groups are introduced (Table 3).<sup>33</sup> Similar patterns of behaviour have been reported<sup>34</sup> for ions of the type [R<sub>n</sub>P(OR)<sub>4-n</sub>]<sup>+</sup> and it is clear that a number of competing

factors are involved in determining the extent of shielding at phosphorus. Both inductive and mesomeric effects may be involved and it has been suggested that the relative importance of each depends in part on the nature of other attached groups.<sup>34</sup> In the case of phenyl substituents the situation may also be complicated by magnetic anisotropy of the benzene ring. A decrease in the chemical shift difference between the alkoxyphosphonium ions and their phosphoryl analogues as the total number of alkoxy-groups on phosphorus increases has been attributed to increasing electron donation to the phosphorus d-orbitals as more oxygen atoms become attached.<sup>34</sup> Our data follow a similar trend (Table 4), although the role of d<sub>π</sub>-p<sub>π</sub> bonding in this effect is not clear. X-Ray diffraction measurements on these quasiphosphonium salts,<sup>17</sup> and on triarylphosphines, their oxides, sulphides, and selenides,<sup>35</sup> show no significant double-bond character in the phenyl-phosphorus bonds. Our kinetic measurements (see below) also show that the inductive effect of attached oxygen atoms is more important than π-interaction of phosphorus with the oxygen lone pairs.

Decompositions of the quasiphosphonium halides in deuteriochloroform follow first-order kinetics (Table 5) and

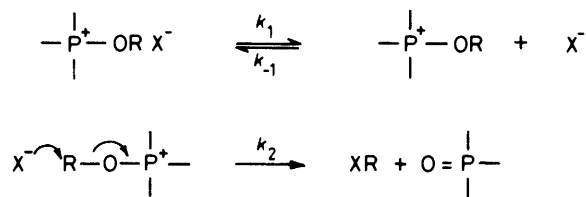
**Table 5.** First-order decomposition of quasiphosphonium halides in  $\text{CDCl}_3$ 

Compound ( $R = \text{Me}_3\text{CCH}_2$ )	$t/^\circ\text{C}$	$10^7 k_1/\text{s}^{-1}{}^a$		
		X = Cl	X = Br	X = I
$\text{Ph}_2\text{P}(\text{OR})\text{MeX}$	33	$1.50 \pm 0.10$	$1.54 \pm 0.06$	$2.75 \pm 0.19$
	60	$92.4 \pm 4.8$	$73.8 \pm 8.3$	$105 \pm 5$
$\text{PhP}(\text{OR})_2\text{MeX}$	33		$114 \pm 4$	$148 \pm 4$
	60		$4\,670 \pm 265$	$5\,260 \pm 540$
$(\text{RO})_3\text{PMeX}$	33		$670 \pm 11$	$1\,100 \pm 40^b$

<sup>a</sup> With 95% confidence limits. <sup>b</sup> Ref. 4.**Scheme 2.**

are thought to proceed by rate-determining collapse to products within the undissociated ion-pair. Alternative schemes involving prior dissociation can be excluded (see below). Absence of rearrangement in the neopentyl group is indicative of 'S<sub>N</sub>2-type' dealkylation (consistent with earlier stereochemical observations in many related reactions)<sup>25</sup> (Scheme 2) although it should be noted that such a reaction is not strictly bimolecular as kinetically separate species are not involved. The decomposition of neopentyloxytriphenylphosphonium chloride in carbon tetrachloride occurs by a similar process which has been described as 'intramolecular S<sub>N</sub>2'.<sup>36</sup> This terminology, however, is questionable and possibly misleading. The transition state (I) is exactly equivalent to that of a conventional S<sub>N</sub>2 process, the only difference being that it is not preceded by the desolvation of separate ions. Earlier suggestions that the formation of alkyl halide occurs directly by a four-centre process from a pentacoordinate species (II)<sup>37,38</sup> or from a closely related 'tight ion-pair' (III)<sup>39,40</sup> in reactions of these types cannot be accepted. Displacement at carbon occurs predominantly if not exclusively with inversion of configuration in both primary and secondary alkyl systems,<sup>23-26,38-42</sup> a result which is geometrically impossible unless the halide ion is separated sufficiently to allow it to make an in-line end-on attack on carbon. Any losses in optical purity which occur are most readily attributable to racemization of the product after formation by halide-halide exchange,<sup>43,44</sup> rather than to a competitive process of substitution with retention. Furthermore, the relatively slow rate at which the neopentyloxyphosphonium derivatives undergo decomposition is entirely in keeping with an inversion process, there being no reason for expecting retentive substitution at C<sub>α</sub> to be slowed by steric hindrance.

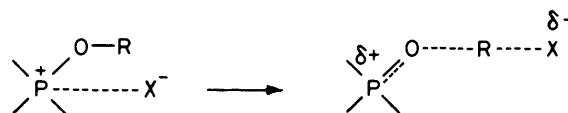
Rate-determining dissociation of the quasiphosphonium halides (Scheme 3,  $k_{-1} \ll k_2$ ) can be excluded, at least for the neopentyloxy-derivatives, since their stability is dependent on the steric resistance of the neopentyl group to S<sub>N</sub>2 attack. In addition, the entropies of activation for such a process might

**Scheme 3.****Table 6.** Activation parameters for first-order decomposition of quasiphosphonium halides in  $\text{CDCl}_3$ 

Compound ( $R = \text{Me}_3\text{CCH}_2$ )	$\Delta H^\ddagger/\text{kcal mol}^{-1}$		
	Cl	Br	I
$\text{Ph}_2\text{P}(\text{OR})\text{MeX}$	$30.3 \pm 0.9$	$28.5 \pm 1.1$	$26.7 \pm 0.9$
$\text{PhP}(\text{OR})_2\text{MeX}$		$27.2 \pm 0.7$	$26.2 \pm 1.0$

Compound ( $R = \text{Me}_3\text{CCH}_2$ )	$\Delta S^\ddagger/\text{cal K}^{-1} \text{mol}^{-1}$		
	Cl	Br	I
$\text{Ph}_2\text{P}(\text{OR})\text{MeX}$	$9.1 \pm 3.1$	$3.4 \pm 3.7$	$-1.4 \pm 2.9$
$\text{PhP}(\text{OR})_2\text{MeX}$		$7.7 \pm 2.3$	$4.8 \pm 3.2$

**Scheme 4.**

be expected to be more clearly positive,<sup>45</sup> whereas those calculated from the observed first-order data are not far from zero; in the case of  $\text{Ph}_2\text{P}(\text{OR})\text{MeI}$  the value is possibly negative (Table 6). These values are presumably associated with a relatively small change in orientation of the ion-pair configuration in which the association of halide ion with the phosphonium centre is replaced by a corresponding association of halide with C<sub>α</sub> in the transition state (Scheme 4). On balance, the net change in the degree of order in the system is small but appears to increase slightly in the direction Cl < Br < I for both the phenylphosphonite and diphenylphosphinite derivatives.

A further alternative which would accord with first-order kinetics consists in the formation of a low steady-state concentration of dissociated ions followed by rate-determining S<sub>N</sub>2 attack (Scheme 3,  $k_2 \ll k_{-1}$ ).<sup>2</sup> Although the extent of dissociation in deuteriochloroform is expected to be small and cannot be determined directly, it may be estimated by calculation from the mean ionic diameter,  $a$ , and the dielectric constant of the medium,  $\epsilon$ , by means of the Fuoss equation (1)<sup>46</sup> where  $b = |z_1 z_2| e^2 / \epsilon k T a$  ( $K$  = dissociation constant,

$$1/K = 4\pi N a^3 e^b / 3000 \quad (1)$$

$N$  = Avogadro number,  $a$  = mean ionic diameter,  $z_1$  and  $z_2$  are the algebraic valencies of cation and anion respectively,  $e$  = protonic charge,  $k$  = Boltzmann's constant,  $T$  = absolute temperature,  $\epsilon$  = dielectric constant of the medium).

This equation has been shown to give good estimates of the dissociation constant for tetraisopentylammonium nitrate in various water-dioxane mixtures.<sup>47</sup> For the purpose of the present calculations we have assumed that the dielectric constant for deuteriochloroform is similar to that published

**Table 7.** Calculated dissociation constants for quasiphosphonium bromides in  $\text{CDCl}_3$  and the activation parameters for a hypothetical rate-determining reaction between kinetically separate ions

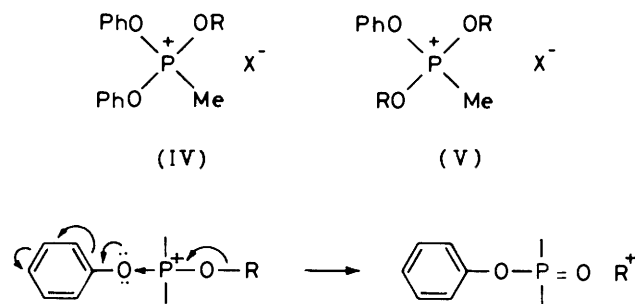
Compound	$t/^\circ\text{C}$	$10^{12}K$	$\Delta H^\ddagger/$ kcal mol $^{-1}$	$\Delta S^\ddagger/$ cal K $^{-1}$ mol $^{-1}$
$\text{Ph}_2\text{P}(\text{OR})\text{MeBr}$	33	22.7	$28.4 \pm 1.1$	$52.5 \pm 3.7$
	60	15.6		
$\text{PhP}(\text{OR})_2\text{MeBr}$	33	7.97	$30.1 \pm 0.7$	$68.0 \pm 8.3$
	60	5.41		

for chloroform<sup>48</sup> and we have taken the minimum interionic distance as determined by X-ray crystallography<sup>17</sup> for the bromides as the mean ionic diameter. The  $K$  values so obtained and the corresponding values of the activation parameters for a hypothetical rate-determining second stage are given in Table 7. Although the  $\Delta H^\ddagger$  values do not differ significantly from those derived from  $k_{\text{obs}}$ , the entropies of activation are large and positive and are inconsistent with a conventional  $S_N2$  process; this mode of reaction can also therefore be excluded.

An interesting feature of the results is that the free energies of activation and/or the rates of decomposition in each of the series are virtually unaffected by the nature of X (Cl, Br, I). A slight increase in activation enthalpy in the direction  $\text{I} < \text{Br} < \text{Cl}$  is offset by a corresponding increase in the entropy of activation. The reactivity order thus lies between that for  $S_N2$  reactions in hydroxylic solvents ( $\text{Cl} < \text{Br} < \text{I}$ )<sup>49</sup> and that which is expected for such reactions in the gas phase ( $\text{Cl} > \text{Br} > \text{I}$ ).<sup>50</sup> Weak solvation of halide ion by the solvent is implied (e.g.  $\text{Cl}_3\text{CH} \cdots \text{X}^-$ ). In a more ionising medium typified by  $\text{CD}_3\text{CN}$ , the reactions deviated from first order in accord with dissociation in this solvent; the overall rate of product formation was also lower, as the separated ions have to meet again before reaction can occur.

The stability and reactivity of quasiphosphonium compounds has been attributed to the extent of  $d_{\pi-p_{\pi}}$  interaction between phosphorus and the non-bonded electrons of attached ligands.<sup>51</sup> In this context, the alkoxy-substituent was considered to be electron-releasing (+M) in contrast to phenoxy which is electron-attracting (-I). Our present results suggest, however, that the over-riding effect of alkoxy in these compounds is inductive (electron-withdrawing). In the series  $\text{Ph}_n\text{P}(\text{OR})_{3-n}\text{MeX}$ , the stability is seen to increase with increasing  $n$ . Mesomeric interaction between phenyl and the phosphorus atom is not supported by bond length measurements which show no evidence of double bond character<sup>17</sup> (cf. also ref. 35). The phenyl-phosphorus bond is in fact marginally longer than the methyl-phosphorus bond in both the phenylphosphonite and diphenylphosphinite adducts. Similar results have been reported for other phosphonium compounds in which both phenyl and methyl are attached to the same phosphorus atom.<sup>52-54</sup> In this case, the replacement of phenyl by alkoxy should have a stabilising effect on quasiphosphonium compounds, if mesomeric electron release from oxygen to phosphorus is a significant factor, whereas exactly the opposite is true.

The electron-withdrawing effect of phenoxy is reflected in the reported stabilities of the quasiphosphonium halides  $\text{Ph}_n\text{P}(\text{OPh})_{4-n}\text{X}$  which increase as phenoxy is replaced by phenyl.<sup>55,56</sup> We have briefly investigated the effect of phenoxy-groups on the mechanism of alkyl-oxygen fission in the reactions of neopentyl diphenyl phosphite and of dineopentyl phenyl phosphite with alkyl halides. In these cases, the Michaelis-Arbuzov intermediates could not be isolated but



Scheme 5.

they are presumably the same as those [(IV), (V)], which may be assumed to occur in Rydon's method for the preparation of alkyl halides from triphenyl phosphite, alkyl halide, and an alcohol.<sup>57</sup> Some disproportionation of the mixed phosphite esters was observed. The formation of a small but detectable amount of tertiary halide in the course of these reactions (Table 8) shows that  $S_N1$ -type fission of R-O may be encouraged by the electron-withdrawing effect of the phenoxy-substituents (Scheme 5). The extent of rearrangement, however, is less than that which has been found to occur<sup>37,58,59</sup> during the preparation of neopentyl halides by Rydon's method in which, it should be noted, phenol is also formed as a by-product. Our results suggest that the presence of phenol itself has a significant effect on the reaction mechanism and hence on the isomeric purity of the halides which are obtained. We have previously reported an increasing extent of rearrangement in secondary alkyl groups as the reaction proceeds in this type of system and have attributed this to the changing polarity of the medium.<sup>31</sup>

## Experimental

**Instrumentation.**—<sup>31</sup>P N.m.r. spectra were recorded on a Bruker HFX90 instrument and <sup>1</sup>H n.m.r. spectra on a Perkin-Elmer R12B spectrometer. Chemical shifts (downfield positive) are given relative to 85% phosphoric acid and to  $\text{Me}_4\text{Si}$ , respectively.

**Starting Materials.**—The following compounds were obtained commercially: chlorodiphenylphosphine (Aldrich) (redistilled; b.p. 126–128 °C at 0.3 mmHg), dichlorophenylphosphine (Albright and Wilson) (redistilled; b.p. 98–104 °C at 0.2 mmHg), phosphorus trichloride (Hopkin and Williams; GPR grade), neopentyl alcohol (Fluka AG; Purum grade), iodomethane (Hopkin and Williams; GPR grade) (redistilled; b.p. 41–43 °C), bromomethane (Hopkin and Williams; Fine Chemicals grade), chloromethane (Matheson).

Phenyl phosphorodichloridite, b.p. 90–92 °C at 11 mmHg,  $n_D^{20}$  1.5621 (Found: Cl, 36.6. Calc. for  $\text{C}_6\text{H}_5\text{Cl}_2\text{OP}$ : Cl, 36.4%),  $\delta_p$  +177.8 p.p.m., and diphenyl phosphorochloridite, b.p. 114–120 °C at 0.2 mmHg,  $n_D^{20}$  1.5759 (Found: Cl, 14.0. Calc. for  $\text{C}_{12}\text{H}_{10}\text{ClO}_2\text{P}$ : Cl, 14.0%),  $\delta_p$  +156.8 p.p.m., were prepared as described,<sup>60,61</sup> the final distillations being performed with a 10 or 20 cm glass-ring fractionating column, respectively.

**Preparation of Neopentyl Diphenylphosphinite.**—Chlorodiphenylphosphine (70.1 g, 0.318 mol) in light petroleum (b.p. 30–40 °C) (25 ml) was added dropwise with stirring to neopentyl alcohol (28.0 g, 0.318 mol) and pyridine (25.2 g, 0.319 mol), also dissolved in light petroleum (10 ml) at 0 °C. The reaction mixture was filtered at room temperature and the solid pyridinium chloride was washed with light petroleum.

**Table 8.** Formation of rearranged alkyl halides in the Michaelis–Arbuzov reactions of neopentyl diphenyl phosphite and of dineopentyl phenyl phosphite

Reactants <sup>a</sup>		Reaction time (days)	Temp. (°C)	Total reaction (%)	Tertiary halide (%)
(RO)(PhO) <sub>2</sub> P	MeI	45	33	73 <sup>b</sup>	0
(RO)(PhO) <sub>2</sub> P	MeBr	240	20–33 <sup>c</sup>	52	4.4
(RO)(PhO) <sub>2</sub> P	MeBr <sup>d</sup>	178	20–33 <sup>e</sup>	39	50
(RO)(PhO) <sub>2</sub> P	PhCH <sub>2</sub> Cl	374	20–100 <sup>f</sup>	55	19.3
(RO) <sub>2</sub> (PhO)P	MeI	4	33	79 <sup>g</sup>	0
(RO) <sub>2</sub> (PhO)P	MeBr	240	20–33 <sup>h</sup>	78	0.1
(RO) <sub>2</sub> (PhO)P	PhCH <sub>2</sub> Cl	343	20–100 <sup>i</sup>	65	0

<sup>a</sup> R = Me<sub>3</sub>CCH<sub>2</sub>. <sup>b</sup> Final residue contained (<sup>31</sup>P n.m.r.) (RO)(PhO)P(O)Me,  $\delta$  + 28 (m) (11%), (PhO)<sub>2</sub>P(O)Me,  $\delta$  + 24 (q) (28%), (RO)(PhO)<sub>2</sub>P,  $\delta$  + 129 (t) (27%), and (PhO)<sub>3</sub>P,  $\delta$  + 128 (s). <sup>c</sup> Days/°C: 90/20 and 150/33. <sup>d</sup> In presence of phenol (1 mol. equiv.). <sup>e</sup> Days/°C: 20/20 and 158/33. <sup>f</sup> Days/°C: 20/20, 51/33, 129/70, and 174/100. <sup>g</sup> Final residue contained (<sup>31</sup>P n.m.r.): (RO)(PhO)P(O)Me,  $\delta$  + 27 (m) (52%), (RO)<sub>2</sub>P(O)Me,  $\delta$  + 30 (m), (RO)<sub>2</sub>(PhO)P,  $\delta$  + 134 (quintet) (21%), (RO)(PhO)<sub>2</sub>P,  $\delta$  + 129 (t) (12%), and unidentified,  $\delta$  + 17 p.p.m.) (3%). <sup>h</sup> Days/°C: 90/20 and 150/33. <sup>i</sup> Days/°C: 20/20, 12/50, 130/70, and 181/100.

After removal of solvent from the combined washings and filtrate under reduced pressure, the crude product (77.0 g) was distilled to give *neopentyl diphenylphosphinite* (56.2 g, 65%) (Found: C, 75.4; H, 7.6; P, 10.9. C<sub>17</sub>H<sub>21</sub>OP requires C, 75.0; H, 7.8; P, 11.3%), b.p. 120–125 °C at 0.05 mmHg,  $n_D^{20}$  1.5622,  $\delta_p$  + 113 p.p.m.

**Preparation of Dineopentyl Phenylphosphonite.**—Dichlorophenylphosphine (35.8 g, 0.200 mol) in light petroleum (b.p. 30–40 °C) (20 ml) was added dropwise with stirring to neopentyl alcohol (35.2 g, 0.400 mol) and pyridine (31.6 g, 0.400 mol) also dissolved in light petroleum (10 ml), at 0 °C. After 2 h, the mixture was filtered and the pyridinium chloride (45.0 g) was washed with light petroleum ether. After removal of solvent by evaporation from the combined washings and filtrate the crude product (54.6 g) was distilled to give *dineopentyl phenylphosphonite* (47.0 g, 81%) (Found: C, 66.4; H, 9.6; P, 10.8. C<sub>16</sub>H<sub>27</sub>O<sub>2</sub>P requires C, 68.0; H, 9.6; P, 11.0%), b.p. 74–80 °C at 0.2 mmHg,  $n_D^{20}$  1.4889,  $\delta_p$  + 154 p.p.m.

**Preparation of Neopentyl Diphenyl Phosphite.**—Diphenyl phosphorochloridite (50.5 g, 0.200 mol) in anhydrous light petroleum (b.p. 30–40 °C) (55 ml) was added dropwise at 0 °C with frequent shaking to neopentyl alcohol (17.6 g, 0.200 mol) and pyridine (15.8 g, 0.200 mol), also dissolved in light petroleum (65 ml). After 13 days at room temperature the pyridinium chloride was filtered off and washed with light petroleum. The solvent was removed from the combined washings and filtrate under reduced pressure and the crude product (56.0 g) was distilled with a 10 cm glass-ring fractionating column to give *neopentyl diphenyl phosphite* (47.0 g, 77%) (Found: C, 66.0; H, 7.1; P, 10.2. C<sub>17</sub>H<sub>21</sub>O<sub>3</sub>P requires C, 67.1; H, 7.0; P, 10.2%), b.p. 138–142 °C at 0.2 mmHg,  $n_D^{20}$  1.5296,  $\delta_p$  + 129 p.p.m. (t,  $J_{POCH}$  5.7 Hz).

**Preparation of Dineopentyl Phenyl Phosphite.**—Phenyl phosphorodichloridite (58.9 g, 0.302 mol) in anhydrous light petroleum (b.p. 30–40 °C) (25 ml) was added dropwise with frequent stirring to neopentyl alcohol (52.9 g, 0.601 mol) and pyridine (49.0 g, 0.620 mol) also dissolved in anhydrous light petroleum (b.p. 30–40 °C) (25 ml), at 0 °C. The mixture was kept at room temperature overnight and the pyridinium chloride was then filtered off and washed with light petroleum. After removal of solvent by evaporation from the combined washings and filtrate the crude product (82.5 g) was fractionally distilled to give *dineopentyl phenyl phosphite* (72.4 g, 82%) (Found: C, 64.5; H, 9.2; P, 10.4. C<sub>16</sub>H<sub>27</sub>O<sub>3</sub>P requires C, 64.4; H, 9.1; P, 10.4%), b.p. 76–82 °C at 0.05 mmHg,  $n_D^{20}$  1.4750,  $\delta_p$  + 134 p.p.m. (quintet,  $J_{POCH}$  6.2 Hz).

**Preparations of Quasiphosphonium Halides.**—Alkyl halides were added to neopentyl diphenylphosphinite or to dineopentyl phenylphosphonite as follows: iodomethane with stirring to an ethereal solution at room temperature; bromomethane to an ethereal solution at –80 °C; chloromethane by condensation of the gas onto the neat ester at 0 °C. The bromide and chloride mixtures were sealed in glass tubes. After specified times at room temperature (Table 1) the products which had precipitated were filtered off, washed with anhydrous ether, and dried *in vacuo*. No phosphonium halide was obtained from dineopentyl phenylphosphonite (1.4 g) and chloromethane (1.0 g); <sup>1</sup>H n.m.r. showed the formation only of the Arbuzov product PhP(O)(OR)Me (*cf.* Table 2) (8% in 3 days at 20 °C; 37% after a further 37 days at 33 °C; 48% after a further 196 days at 70 °C). Similarly, trineopentyl phosphite (0.9 g) and chloromethane (0.9 g) gave dineopentyl methylphosphonate,  $\delta_p$  + 28 p.p.m. during 12 h at 50–60 °C and 172 h at 70–80 °C, no phosphonium intermediate being detectable.

**Reactions of Neopentyl Diphenyl Phosphite and of Dineopentyl Phenyl Phosphite with Alkyl Halides.**—Equimolar amounts of the ester and the halide (Table 8) were in each case sealed in a <sup>1</sup>H n.m.r. tube and the extent of reaction was monitored periodically by following the formation of CH<sub>3</sub>–P doublets ( $J_{PCH}$  15–20 Hz) due to (RO)(PhO)P(O)Me ( $\delta$  1.49), (RO)<sub>2</sub>P(O)Me ( $\delta$  1.34), and (PhO)<sub>2</sub>P(O)Me ( $\delta$  1.61), or the formation of doublets ( $J_{PCH}$  23–24 Hz) due to the benzylic protons of (RO)(PhO)P(O)CH<sub>2</sub>Ph ( $\delta$  3.19), (RO)<sub>2</sub>P(O)CH<sub>2</sub>Ph ( $\delta$  3.07), and (PhO)<sub>2</sub>P(O)CH<sub>2</sub>Ph ( $\delta$  3.10). The temperature was gradually increased, if necessary, to bring about the reaction. The volatile products (pentyl halides) and excess of methyl halide were finally removed at room temperature under reduced pressure, trapped (–80 °C), and analysed by g.l.c.<sup>62</sup>

**Kinetics of Decomposition of Quasiphosphonium Halides.**—(a) *In* CDCl<sub>3</sub> at 33 °C. The quasiphosphonium halide (*ca.* 0.1 g) was dissolved in anhydrous CDCl<sub>3</sub> (1.0 ml) to give a solution containing *ca.* 0.3 mol l<sup>-1</sup> and the mixture was sealed into a <sup>1</sup>H n.m.r. tube. The n.m.r. tube was placed in a thermostatted bath at 33 °C and was periodically transferred to the n.m.r. spectrometer, also at 33 °C. Spectra were normally recorded 20 min after mixing and then every few hours or days according to reaction rate until 80–90% of the reaction had been completed. The decreasing doublet due to the methyl protons adjacent to phosphorus in the phosphonium halide and the increasing doublet due to the methyl protons adjacent to phosphorus in the Arbuzov product (*cf.* Table 2) were used to determine the composition of the reaction mixture.

(b) In  $\text{CDCl}_3$  at  $60^\circ\text{C}$ . The quasiphosphonium compound (0.5–0.6 g) was dissolved in anhydrous  $\text{CDCl}_3$  (5 ml) to give a solution containing ca.  $0.3\text{ mol l}^{-1}$ . The solution was divided into seven equal portions which were sealed into separate  $^1\text{H}$  n.m.r. tubes. The tubes were placed in an oil-bath thermostatted at  $60^\circ\text{C}$ . At suitable intervals (every few minutes or hours according to reaction rate), an n.m.r. tube was taken from the oil-bath, cooled rapidly in a Cardice-acetone mixture ( $-80^\circ\text{C}$ ) and then allowed to warm to  $33^\circ\text{C}$  in the n.m.r. spectrometer. Without delay, the  $^1\text{H}$  n.m.r. spectrum was recorded.

Graphs of  $\log_{10}(a/a-x)$  against time and of  $x/a(a-x)$  against time were plotted and in all cases the decompositions were seen to follow first-order kinetics (Table 5).

(c) In  $\text{CD}_3\text{CN}$  at  $33^\circ\text{C}$ . The quasiphosphonium salts were significantly more stable in  $\text{CD}_3\text{CN}$  than in  $\text{CDCl}_3$ . Thus, at  $33^\circ\text{C}$ , the concentration ( $\text{mol l}^{-1}$ ) of methyl(dineopentylphenoxy)phenylphosphonium iodide fell from 0.270 to 0.135 in 110 h (cf.  $t_{1/2}$  13.0 h in  $\text{CDCl}_3$ ), whilst that of the bromide fell from 0.456 to 0.225 in 71 h (cf.  $t_{1/2}$  16.9 h in  $\text{CDCl}_3$ ). Kinetic plots showed deviations from first-order behaviour. Although accurate determinations of the order were not possible, plots of  $\log(-dc/dt)$  against  $\log c$  indicated reaction orders of between one and two.

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