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QUASIPHOSPHONIUM INTERMEDIATES—IV[1]

ISOLATION AND IDENTIFICATION OF INTERMEDIATES IN THE ARBUZOV AND PERKOW REACTIONS OF NEOPENTYL ESTERS OF PHOSPHORUS(III) ACIDS WITH α-HALOGENOACETOPHENONES

IMRE PETNEHÁZY, GYONGYI SZAKÁL and LÁSZLÓ TŐKE*
Department of Organic Chemical Technology, Technical University Budapest, 1521 Budapest, Müegyetem, Hungary

HARRY R. HUDSON* and LUBA POWROZNYK
School of Chemistry, The Polytechnic of North London, Holloway Road, London N7 8DB, England

and

CHRISTOPHER J. COOKSEY
Department of Chemistry, University College London, 20 Gordon Street, London WC1H OAJ, England

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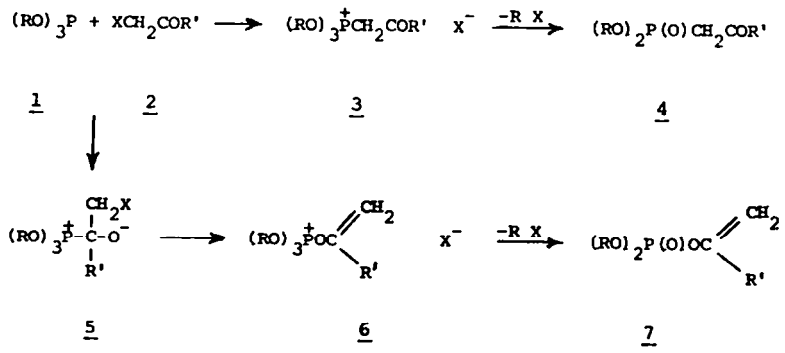
Abstract—Crystalline ketophosphonium bromides have been isolated as intermediates in the reactions of trineopentyl phosphite, dineopentyl phenylphosphonite, and neopentyl diphenylphosphinite with α-bromoacetophenone. Thermal decomposition in solution occurs in each case to yield neopentyl bromide and the corresponding Arbuzov product only. Rearrangement to the Perkow intermediate or product does not occur. An identifiable Perkow intermediate was separated from the reaction of neopentyl diphenylphosphinite with α-chloroacetophenone at 0° and was shown to yield neopentyl chloride and the corresponding Perkow product by a first-order process in chloroform ($t_{1/2}$ *ca* 40 min at 33°). It is suggested that the betaine formed by initial attack of phosphorus at the carbonyl carbon atom may be a common first intermediate in reactions that yield both Arbuzov and Perkow products.

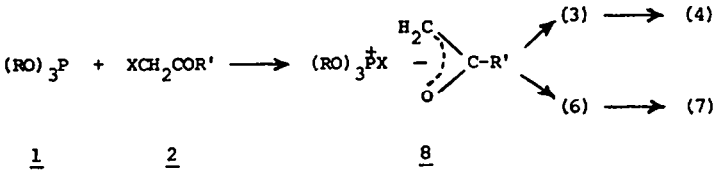
The reactions of trialkyl phosphites with α-halogenocarbonyl compounds yield either ketophosphonates (Arbuzov reaction) or vinyl phosphates (Perkow reaction), according to the halogen present and the reaction conditions.[2] Other phosphorus(III) esters behave similarly.[3] In general it is believed that the Arbuzov product **4** results from initial attack by phosphorus at the α-carbon atom, whereas the Perkow product **7** is formed by initial attack at the carbonyl carbon atom, followed by migration of phosphorus from carbon to oxygen (Scheme 1).[4]

Recent kinetic studies on the reactions of trimethyl phosphite with substituted α-halogenoacetophenones indicate, however, that a common first intermediate may be involved in both reaction pathways.[5] The possibility of initial attack by phosphorus at the α-halogeno substituent to form a halogenophosphonium-enolate ion-pair (**8**), which then rearranges to yield the Arbuzov and Perkow intermediates and products (Scheme 2), was previously discounted, although there is now good evidence that attack at halogen may occur in the reactions of phosphorus(III) esters with α,α - dibromoacetophenones, α - bromo - α - phenylacetophenones, and α-bromoacetophenones that are sterically hindered to attack at the carbonyl centre.[6,7] It has also been suggested elsewhere[8] that the ketophosphonium intermediate (**3**) could give rise to both Arbuzov and Perkow products, the latter being formed after rearrangement *via* a four-membered cyclic phosphorane (**9**).

The only intermediates that have been observed directly in reactions of these types occur during the Perkow reaction of chloral with triethyl phosphite or



Scheme 1.



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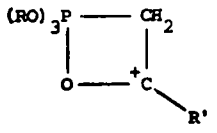
Scheme 2.



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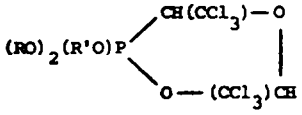

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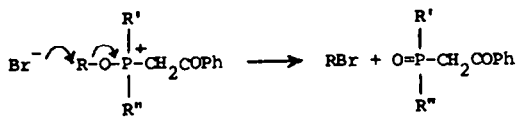
ethyl ethylene phosphite and give rise to high field ^{31}P NMR signals ($\delta -41$ to -42 ppm).[9] These intermediates appear to be 2:1 adducts **10** (R = Et or CH_2; R' = Et) resulting from reaction of the intermediate betaine, $(RO)_2(R'O)\overset{+}{P}CH(CCl_3)O^-$, with a second molecule of chloral, although the betaine itself and the vinyloxyphosphonium intermediate to which it is assumed to rearrange before yielding the vinyl phosphate have not been identified.

RESULTS AND DISCUSSION

We now report the first examples of ketophosphonium and vinyloxy-phosphonium halides to be isolated as intermediates in the reactions of phosphorus(III) esters with α-halogenocarbonyl compounds.[10] Trineopentyl phosphite, dineopentyl phenylphosphonite, and neopentyl diphenylphosphinite each underwent reaction with α-bromoacetophenone in acetone, chloroform, or ether to yield the corresponding ketophosphonium bromides (**11–13**) which were separated as crystalline solids, washed with anhydrous ether, dried *in vacuo*, and identified by elemental analysis and NMR spectroscopy. NMR spectroscopic data for the isolated intermediates and for their products of decomposition are shown in Table 1. Although the ^{31}P and ^1H NMR spectra of reactant mixtures showed in each case that both Arbuzov and Perkow routes were followed (Table 2) it was only the more stable Arbuzov intermediates that were precipitated by the removal of solvent and addition of ether.

The rates of formation of the intermediates and their stabilities increased as alkoxy groups were replaced by phenyl,[1,11] neopentyloxy(phenacyl)diphenylphosphonium bromide (**13**) being sufficiently stable for X-ray crystal structure determination to be possible.[12] Even trineopentyloxy(phenacyl)phosphonium bromide (**11**) could be stored under anhydrous ether for several days without significant change. The compounds were also surprisingly resistant to attack by atmospheric moisture.

Decomposition of the ketophosphonium bromides in deuterochloroform or in acetone-d_6 occurred by S_N2-cleavage of the alkyl-oxygen bond (Scheme 3) to give neopentyl bromide and the corresponding Arbuzov products (**15–17**), characterized in each case by a doublet in the ^1H NMR spectrum (J 15–22 Hz) due to the phosphorus-bonded CH_2 group; no signals indicative of vinyl protons were detectable. Even in acetone-acetic acid mixtures, in which trineopentyl phosphite and α-bromoacetophenone were shown to give dineopentyl 1-phenylvinyl phosphate (**18**) as the major product, trineopentyloxy(phenacyl)phosphonium bromide gave only the ketophosphonate (**19**). Similar results were also obtained in acetonitrile containing an equimolar quantity of tetra-n-butylammonium chloride, no Perkow product being formed. Rearrangement of the Arbuzov intermediate to give the Perkow product by way of a cyclic phosphorane



11 - 13 15 - 17

[R' = R" = RO(11,15); R' = RO, R' = Ph(12,16); R' = R" = Ph(13,17); R=Me_3CCH_2]

Scheme 3.

Table 1. NMR data for Arbuzov and Perkow intermediates and products

Structure [a]		^{31}P	^{1}H δ (ppm)					J (Hz)	
		δ (ppm)	Me_3C	CH_2OP	CH_2-P	CH_2=C	Ph	POCH	PCH
$(RO)_3\overset{+}{P}CH_2COPh\ Br^-$	**11**	+ 41.0	1.02(s)	4.35(d)	5.74(d)	-	7.3-8.4(m)	4.8	18.3
$PhP\overset{+}{}(OR)_2CH_2COPh\ Br^-$	**12**	+ 67.1	1.07(s)	4.34(m)[b]	5.99(d)	-	7.2-8.4(m)	[b]	15.6
$Ph_2P\overset{+}{}(OR)CH_2COPh\ Br^-$	**13**	+ 68.3	0.99(s)	4.15(d)	6.25(d)	-	7.2-8.3(m)	4.2	12.6
$Ph_2P\overset{+}{}(OR)OC(:CH_2)Ph\ Cl^-$	**14**	+ 55.9	0.98(s)	4.04(d)	-	5.48(m)	7.3-8.2(m)	4.8	-
$(RO)_2P(O)CH_2COPh$	**15**	+ 19.0	0.86(s)	3.72(d)	3.65(d)	-	7.2-8.1(m)	4.8	22.8
$PhP(O)(OR)CH_2COPh$	**16**	+ 32.1	0.81(s)	3.52(m)[c]	3.77(dd)[d]	-	7.3-8.3(m)	[c]	[d]
$Ph_2P(O)CH_2COPh$	**17**	+ 28.2	-	-	4.14(d)	-	7.3-8.5(m)	-	15.6
$(RO)_2P(O)OC(:CH_2)Ph$	**18**	- 7.0	0.95(s)	3.78(d)	-	5.30(m)	7.2-8.1(m)	4.8	-
$PhP(O)(OR)OC(:CH_2)Ph$	**19**	+ 15.0	0.89(s)	3.77(d)	-	5.19(d)	7.2-8.2(m)	5.1	-
$Ph_2P(O)OC(:CH_2)Ph$	**20**	+ 29.7	-	-	-	5.15(m)	7.2-8.2(m)	-	-

[a] R = Me_3CCH_2. [b] Doublet of AB patterns: $\delta(H_A)$ 4.42, $\delta(H_B)$ 4.26 ppm, J_{AB} 8.0, $J_{POCH(A)}$ 4.0, $J_{POCH(B)}$ 4.1 Hz. [c,d] Complex overlapping signals consisting of a doublet of AB patterns (CH_2OP), $\delta(H_A)$ 3.67, $\delta(H_B)$ 3.37 ppm, J_{AB} 8.9, $J_{POCH(A)}$ 5.1, $J_{POCH(B)}$ 4.8 Hz, and a doublet of doublets (CH_2P), $\delta(H_A)$ 3.79, $\delta(H_B)$ 3.74 ppm, J_{AB} 0, $J_{POCH(A)}$ 18.4, $J_{POCH(B)}$ 17.5 Hz. The CH_2P signal could be removed and hence identified by shaking with D_2O for several hours.

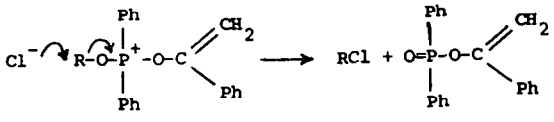
Table 2. Reaction products and intermediates observed during the interaction of phosphorus(III) esters with α-halogenoacetophenones[a]

Ester[b]	Halide	Reaction time (h)	Unreacted ester (%)	Arbuzov Int. (%)	Arbuzov Prod. (%)	Perkow Int. (%)	Perkow Prod. (%)
$(RO)_3P$	$PhCOCH_2Br$[c]	0.92	31	15	23	0	31
"	"	23.5	0	5	49	0	46
$(RO)_3P$	$PhCOCH_2Br$[d]	168	0	0	74	0	26
$(RO)_3P$	$PhCOCH_2Br$[e]	1.33	0	0	0	0	100
$(RO)_3P$	$PhCOCH_2Cl$[c]	2.5	2	0	0	0	98
$PhP(OR)_2$	$PhCOCH_2Br$[c]	[f]	2	41	0	0	57
$PhP(OR)_2$	$PhCOCH_2Cl$[c]	[f]	0	0	0	0	100
Ph_2POR	$PhCOCH_2Br$[c]	0.25	8	68	0	10	13
Ph_2POR	$PhCOCH_2Cl$[c]	0.17	20	0	0	35	45

[a] At room temperature. [b] R = Me_3CCH_2. [c] In $CDCl_3$. [d] In acetone-d_6; product composition based on integration of proton-coupled ^{31}P n.m.r. spectrum; the ^1H signal due to the α-CH_2 of the ketophosphonate slowly disappears in this solvent because of deuterium-exchange. [e] In a mixture of acetone-d_6 (90%) and acetic acid-d (10%). Final product, δ_P -7.2 ppm (quintet). During the first 2 min of reaction an initial signal at δ_P -7.4 was quickly replaced by the product signal at δ_P -7.2 and is tentatively assigned to the vinyloxyphosphonium species (Perkow intermediate). [f] Spectrum recorded immediately after mixing.

intermediate (**9**)[8] or other route is therefore excluded under the conditions of these experiments.[13]

Perkow intermediates are evidently less stable. Thus the reactions of trineopentyl phosphite and of dineopentyl phenylphosphonite in $CDCl_3$ with α-chloroacetophenone gave only the corresponding Perkow products (**18**, **19**), the intermediates not being detectable at any stage (Table 2). A Perkow intermediate was nevertheless detected in the reaction of neopentyl diphenylphosphinite with α-chloroacetophenone and was separated as a solid product after reaction in chloroform at −5 to 0° by evaporation of the chloroform and the addition of dry ether. The intermediate (**14**) could be stored below 0° in the absence of moisture but it decomposed to yield 1-phenylvinyl diphenylphosphinate (**20**) when redissolved in deuterochloroform ($t_{1/2}$ *ca* 40 min at 33°). As in the decomposition of the ketophosphonium bromides, the exclusive formation of neopentyl halide is indicative of S_N2-type dealkylation (Scheme 4).[14]



14 **20**

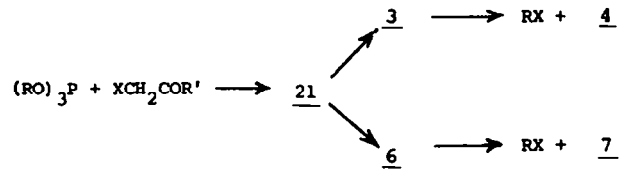
Scheme 4.

In the reaction of trineopentyl phosphite with α-bromoacetophenone the vinyl phosphate (**18**) was seen to be the major product in the initial stages of the reaction but the product ratio changed in favour of the ketophosphonate (**15**) as the reaction proceeded and the ketophosphonate (as expected) was ultimately the major product. This effect results from the greater stability of the Arbuzov intermediate (**11**) (only noticeable in the reactions of sterically hindered esters such as neopentyl), so that the concentration of this intermediate builds up initially whilst the Perkow route proceeds more rapidly to products.

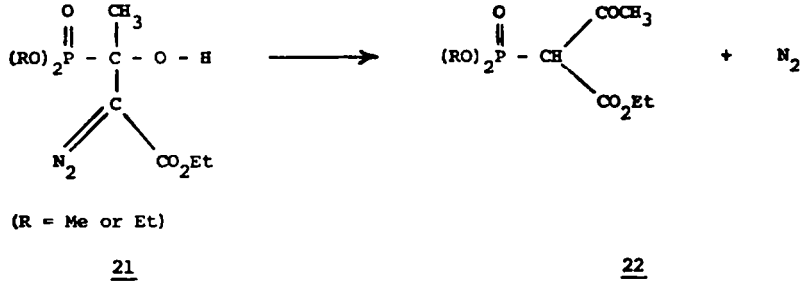
The overall results, together with previous kinetic studies,[5] are consistent with a reaction scheme in which the Arbuzov and Perkow products are formed by parallel pathways from a common first intermediate (**21**) (Scheme 5).

The identity of such an intermediate[5] is still not clear although the ketophosphonium halide and the halogenophosphonium-enolate ion pair[7] can be excluded in the examples that we have investigated. A possible candidate is the betaine **5**; this could then yield the Arbuzov product by 1,2-migration of the phosphite moiety to the α-carbon atom or the Perkow product by intramolecular rearrangement as previously described.[4] A similar 1,2-migration of phosphorus has been reported in the decomposition of the diazo derivative **21**, either thermally or in the presence of acid, to yield the ketophosphonate **22** in 90% yield (Scheme 6).[15]

Evidence for betaine formation in the Perkow reaction has been provided by various workers,[4,9,16] and it has been assumed that it is the *O*-protonated betaine which



Scheme 5.



Scheme 6.

undergoes dealkylation to yield α-hydroxyphosphonate when trialkyl phosphites react with α-halogenocarbonyl compounds in acid conditions.[4]

Hammett plots for the parallel formation of Perkow and Arbuzov products in the reactions of trimethyl phosphite with substituted α-bromoacetophenones (ρ = 1.36 in toluene at 70°)[5] are consistent with initial attack at carbonyl carbon. For the pure Perkow reactions of trimethyl phosphite with substituted α-chloroacetophenones under similar conditions, the ρ value is 1.62.[5] A similar difference has previously been reported for the Perkow reactions in benzene (44.9°) of triethyl phosphite with α-chloroisobutyrophenone (ρ = 1.89) and with α-chloroisobutyrophenone (ρ = 2.37), for which rate-determining attack of the phosphite at carbonyl carbon was proposed.[16] Significantly lower ρ values are associated with S_N2 displacement of bromide from the α-carbon atom of α-bromoacetophenones, e.g. +0.44 for reaction with triphenylphosphine and +0.30 for reaction with pyridine in nitromethane at 34.9°.[17]

EXPERIMENTAL

Trineopentyl phosphite, dineopentyl phenylphosphonite, and neopentyl diphenylphosphinite were prepared as described.[1,18] α-Chloroacetophenone and α-bromoacetophenone were obtained commercially. ^{31}P NMR spectroscopy was carried out on a Varian CFT-20 spectrometer operating at 32.4 MHz. ^{1}H and ^{13}C NMR spectra were recorded on Perkin–Elmer R12B (60 MHz) and Jeol 100 MHz instruments. Chemical shifts are given relative to 85% H_3PO_4(^{31}P) and to TMS (^{1}H and ^{13}C) (downfield positive). Reactions in NMR tubes were monitored at ambient temperature after adding equivalent quantities of the α-halogenoketones to solutions (*ca* 20% w/v) of the phosphorus(III) esters in the specified solvents (Table 2). Quantitative data are based on continuous wave ^{1}H NMR spectroscopy.

Isolation of intermediates

(a) *From trineopentyl phosphite and α-bromoacetophenone.* Solutions of trineopentyl phosphite (3.0 g, 10.2 mmol) in acetone (2 cm^3) and α-bromoacetophenone (2.5 g, 12.6 mmol) in acetone (6 cm^3) were mixed at room temperature. After 1.5 h the acetone was removed under reduced pressure and anhydrous ether was added. The white crystalline product that was precipitated was filtered off, washed with ether, and dried *in vacuo* to give trineopentyloxy(phenacyl)phosphonium bromide (**11**) (0.6 g, 12%) (Found: C, 56.8; H, 8.1. $C_{23}H_{40}BrO_4P$ requires: C, 56.2; H, 8.2%), m.p. (sealed tube) 85–86°, δ_p ($CDCl_3$) + 41 ppm, δ_H ($CDCl_3$) 1.02 (s, Me_3C), 4.35 (d, CH_2OP, J_{POCH} 4.8 Hz), 5.74 (d, CH_2P, J_{PCH} 18.3 Hz), 7.3–8.4 (m, Ar). In a similar preparation, trineopentyl phosphite (3.3 g, 11.3 mmol) and α-bromoacetophenone (2.5 g, 12.6 mmol) were allowed to interact for 3 h. After removal of acetone and the addition of ether, the mixture was first cooled to 0° and then maintained at 16° overnight to yield crystals of the same intermediate **11** (1.1 g, 20%) (Found: Br, 16.2. Calc for $C_{23}H_{40}BrO_4P$: Br, 16.3%), m.p. (sealed tube) 83–84°.

(b) *From dineopentyl phenylphosphonite and α-bromoacetophenone.* α-Bromoacetophenone (2.6 g, 13.1 mmol) in ether (25 cm^3) was added with stirring to dineopentyl phenylphosphonite (3.7 g, 13.1 mmol) in ether (1 cm^3) at 16°. Crystals started to separate after 10 min and were collected as two crops which were washed with ether and dried *in vacuo*: (a) 0.7 g, m.p. (sealed tube) 122° (after 1.5 h); (b) 1.3 g, mp (sealed tube) 122° (after a further 18 h). The combined product was identified as dineopentyloxy(phenacyl)phenylphosphonium bromide (**12**) (total yield 2.0 g, 32%) (Found: C, 59.2; H, 7.1; Br, 16.4. $C_{24}H_{34}BrO_3P$ requires: C, 59.9; H, 7.1; Br, 16.6%), δ_p($CDCl_3$) + 67.1 ppm, δ_H($CDCl_3$) 1.07 (s, Me_3C), 4.34 [d AB, CH_2OP, $\delta(H_A)$ 4.42, $\delta(H_B)$ 4.26, J_{AB} 8.0, $J_{POCH(A)}$ 4.0, $J_{POCH(B)}$ 4.1 Hz], 5.99 (d, CH_2P, J_{PCH} 15.6 Hz), 7.2 – 8.4 (m, Ar).

(c) *From neopentyl diphenylphosphinite and α-bromoacetophenone.* α-Bromoacetophenone (1.5 g, 7.5 mmol) in the minimum of dry acetone (5 cm^3) was added dropwise to neopentyl diphenylphosphinite (2.0 g, 7.35 mmol) with cooling in ice-water (the reaction is strongly exothermic). After 15 min the crystals which had separated were filtered off and washed with dry ether to give neopentyloxy(phenacyl)diphenylphosphonium bromide (**13**) (1.36 g, 39%) (Found: C, 63.1; H, 6.0; Br, 16.0. $C_{25}H_{28}BrO_2P$ requires: C, 64.0; H, 6.0; Br, 17.0%), mp (sealed tube) 146–148°C,

δ_P($CDCl_3$) + 68.3 ppm, δ_H ($CDCl_3$) 0.99 (s, Me_3C), 4.15 (d, CH_2OP, J_{POCH} 4.2 Hz), 6.25 (d, CH_2P, J_{PCH} 12.6 Hz), 7.2–8.5 (m, Ar). A second crop of crystals (0.23 g) m.p. (sealed tube) 153°C, had identical spectral properties. In a similar preparation with chloroform (4.5 cm^3) as the solvent, α-bromoacetophenone (1.4 g, 7.04 mmol) and neopentyl diphenylphosphinite (1.95 g, 7.17 mmol) yielded a precipitate which after 3 h was filtered off, washed with ether, and dried to give white crystals of the same intermediate (**13**) containing 1 molecule of chloroform of crystallisation (2.4 g, 58%) (Found: C, 53.1; H, 5.1. $C_{26}H_{29}Cl_3BrO_2P$ requires: C, 52.8; H, 4.9%), mp (sealed tube) 135–136°C (143°C after recrystallisation from $CHCl_3$). The ^1H NMR spectrum ($CDCl_3$) showed an additional peak, δ7.2 (1H), assigned to $CHCl_3$.

(d) *From neopentyl diphenylphosphinite and α-chloroacetophenone.* α-Chloroacetophenone (1.13 g, 7.31 mmol) in chloroform (2.5 cm^3) was added slowly with shaking at −5 to 0° to neopentyl diphenylphosphinite (2.0 g, 7.35 mmol). The mixture was then concentrated under reduced pressure and dry ether (15 cm^3) added. The oily product that separated was washed with ether by decantation and stored under ether at −6°C for two days when it solidified. The product was characterised by NMR as neopentyloxydiphenyl-1-phenylvinyloxyphosphonium chloride (**14**), δ_P($CDCl_3$) + 55.9 ppm, δ_H ($CDCl_3$) 0.98 (Me_3C, s), 4.04 (CH_2OP, d, J_{POCH} 4.8 Hz), 5.48 (CH_2=C, m), containing minor quantities of unreacted α-chloroacetophenone (δ4.6, s) and acetophenone (δ2.58, s), the latter probably arising from hydrolysis of the phosphonium salt. Further purification was not possible.

Thermal decomposition of intermediates

(a) *Arbuzov intermediates.* Trineopentyloxy(phenacyl)phosphonium bromide (**11**) was dissolved in (i) acetone-d_6, (ii) CD_3CN containing tetra-n-butylammonium chloride (1 mol. equiv.), (iii) a mixture of acetone-d_6 (90%) and acetic acid-d (10%), and (iv) deuterochloroform. Decomposition at room temperature occurred in each case during several hours to give the ketophosphonate (**15**), δ_P + 18.4 to + 19.9 ppm, and neopentyl bromide [δ_H 1.02(s), 3.25(s)] only. Dineopentyloxy(phenacyl)phenylphosphonium bromide (**12**) and neopentyloxy (phenacyl)diphenylphosphonium bromide (**13**) were stable over a long period of time in $CDCl_3$ at room temperature. On heating the solutions in sealed tubes (0.5 h at 100°) both decomposed completely, **12** to give the ketophosphinate (**16**) and **13** to give the phosphine oxide (**17**) as the only phosphorus-containing products. Neopentyl bromide was also formed in each case.

(b) *Perkow intermediate.* The decomposition of neopentyloxydiphenyl-1-phenylvinyloxyphosphonium chloride (**14**) in $CDCl_3$ was monitored at 33° by following the replacement of ^1H NMR signals at δ5.48 (CH_2=C, m) and 4.04 ($Me_3C\underline{CH_2}$, d) by signals at δ5.15 (CH_2=C, m) of the vinyl phosphinate (**20**) and at δ3.26 (CH_2, s) of neopentyl chloride [δ0.96(s), 3.26(s)] ($t_{1/2}$ = *ca* 40 min).

Isolation and characterization of Arbuzov products (**15–17**)

(a) Trineopentyl phosphite (8.76 g, 30 mmol) in acetonitrile (15 cm^3) was added dropwise to a solution of α-bromoacetophenone (3.97 g, 20 mmol) in acetonitrile (15 cm^3) at reflux temperature. The mixture was heated under reflux for a further period of 4 h, after which the solvent was removed under reduced pressure and the residue was distilled to yield dineopentyl phenacylphosphonate (**15**) (3.18 g, 47%) (Found: C, 63.5; H, 8.95. $C_{18}H_{29}O_4P$ requires: C, 63.5; H, 8.6%), b.p. 149–150° at 0.04 mm Hg, n_D^{25} 1.4983, δ_P ($CDCl_3$) + 19.0 ppm, δ_H ($CDCl_3$) 0.86 (Me_3C, s, 18H), 3.72 (CH_2OP, d, 4H, J_{POCH} 4.8 Hz), 3.65 (CH_2P, d, 2H, J_{PCH} 22.8 Hz), 7.50 (Ar, m, 3H), 8.04 (Ar, m, 2H), δ_C($CDCl_3$) 25.89 (CH_3), 32.00 (Me_3C, d, J_{POCC} 7.3 Hz), 37.86 (PCH_2, d, J_{PC} 129.4 Hz), 75.84 (CH_2OP, d, J_{POC} 7.4 Hz), 128.49, 128.95, 133.45, 136.58 (Ar), 191.43 (CO, d, J_{PCC} 6.7 Hz), *m/z* 340 (42%, M^+), 201 (100%), IR $\nu_{C=O}$ 1680, $\nu_{P=O}$ 1270, ν_{POC} 1050, 1010 cm^{-1}.

(b) Dineopentyloxy(phenacyl)phenylphosphonium bromide (**12**; 1.2 g, 2.5 mmol) in $CDCl_3$ (4 cm^3) was heated (0.5 h) in three sealed NMR tubes at 100–105°. Evaporation of the volatile components from the combined products then left a white solid (0.7 g) which was recrystallised from diethyl ether/petroleum (b.p. 40–60°) to give white needles of neopentyl phenacyl(phenyl)phosphinate (**16**; 0.48 g, 58%) (Found: C, 68.8; H, 7.1. $C_{19}H_{23}O_3P$ requires: C, 69.1; H, 7.0%), m.p. 82–83°, δ_P ($CDCl_3$) + 32.1 ppm, δ_H ($CDCl_3$) 0.81 (Me_3C, s, 9H), 3.52 (CH_2OP, d AB, $\Delta\nu_{AB}$ 18 Hz, J_{AB} 8.9, $J_{POCH(A)}$ 5.1, $J_{POCH(B)}$ 4.8 Hz) (overlapping with 3.77 (PCH_2, dd, $\Delta\nu_{AB}$ 3 Hz, J_{AB} 0, $J_{POCH(A)}$ 18.4, $J_{POCH(B)}$ 17.5 Hz) (4H total), 7.3–8.3 (Ar, m, 10H), *m/z* 330 (10%, M^+), 261 (100%), IR (KBr disc) $\nu_{C=O}$ 1667, $\nu_{P=O}$ 1219, ν_{POC} 1031 cm^{-1}.

(c) Neopentyloxy(phenacyl)diphenylphosphonium bromide (**13**; 0.66 g, 1.4 mmol) in deuterochloroform (4.5 cm^3) was heated (0.5 h) in three sealed NMR tubes at 100–105°. Evaporation of the volatile components under reduced pressure then left a white solid residue of phenacyl(diphenyl)phosphine oxide (**17**)[3b] (0.4 g, 89%), δ_P ($CDCl_3$) + 28.2 ppm, δ_H 4.14 (CH_2P, d, J_{PCH} 15.6 Hz, 2H), 7.3–8.5 (Ar, m, 15H), *m/z* 320 (27%, M^+), 201 (100%), IR (KBr disc) $\nu_{C=O}$ 1680, $\nu_{P=O}$ 1184 (lit.[3b] 1190) cm^{-1}. The product was recrystallised from chloroform/diethyl ether to give fine white needles of **17** (Found: C, 75.5; H, 5.5. Calc for $C_{20}H_{17}O_2P$: C, 75.0; H, 5.35%), m.p. 138–140° (lit[3b] mp 140–140.5°).

Isolation and characterization of Perkow products (**18–20**)

(a) Trineopentyl phosphite (8.76 g, 30 mmol) in benzene (15 cm^3) was added dropwise to a solution of α-chloroacetophenone (3.09 g, 20 mmol) in benzene (15 cm^3) at reflux temperature. The mixture was heated under reflux for a further period of 12 h, after which the solvent was removed under reduced pressure and the residue was distilled to give dineopentyl-1-phenylvinyl phosphate (**18**; 5.51 g, 81%) (Found: C, 63.5; H, 9.2. $C_{18}H_{29}O_4P$ requires: C, 63.5; H, 8.6%), b.p. 145–146° at 0.15 mmHg, n_D^{25} 1.4773, δ_P ($CDCl_3$) − 7.0 ppm, δ_H ($CDCl_3$) 0.95 (Me_3C, s, 18H), 3.78 (CH_2O, d, 4H, J_{POCH} 4.8 Hz), 5.30 (CH_2=C, m, 2H), 7.34 (Ar, m, 3H), 7.48 (Ar, m, 2H), δ_C ($CDCl_3$) 25.97 (CH_3), 32.17 (Me_3C, d, J_{POCC} 8.5 Hz), 77.55 (CH_2OP, d, J_{POC} 6.1 Hz), 97.49 (CH_2=, d, J_{POCC} 3.8 Hz), 125.19, 128.35, 129.04, 134.32 (Ar), 152.38 (O–C=, d, J_{POC} 7.3 Hz, *m/z* 340 (10%, M^+), 199 (100%), IR $\nu_{C=C}$ 1630, $\nu_{P=O}$ 1280, ν_{POC} 1060, 1020 cm^{-1}.

(b) α-Chloroacetophenone (5.56 g, 36.0 mmol) in dry chloroform (15 cm^3) was added dropwise to a stirred solution of dineopentyl phenylphosphonite (10.5 g, 37.2 mmol) in dry chloroform (8 cm^3) at 0 to 5°. The mixture was then stirred at 25° (1 h) and left to stand at room temperature for 48 h. Solvent was then removed under reduced pressure to leave a liquid residue (11.5 g) which was distilled to give neopentyl 1-phenylvinyl phenylphosphonate (**19**) (2.0 g, 17%) (Found: C, 69.1; H, 7.0. $C_{19}H_{23}O_3P$ requires: C, 69.1; H, 7.0%), b.p. 184–190° at 0.1 mmHg, n_D^{20} 1.5420, δ_P ($CDCl_3$) + 15.0 ppm, δ_H ($CDCl_3$) 0.89 (Me, s, 9H), 3.77 CH_2O, d, 2H, J_{POCH} 5.1 Hz), 5.19 (CH_2=C, d, 2H), 7.2–8.2 (Ar, m, 10H), *m/z* 330 (9%, M^+), 105 (100%), IR $\nu_{C=C}$ 1622, $\nu_{P=O}$ 1260, ν_{POC} 990–1040(br.) cm^{-1}.

(c) α-Chloroacetophenone (2.25 g, 14.6 mmol) in dry chloroform (4 cm^3) was added quickly with stirring to neopentyl diphenylphosphinite (4.0 g, 14.7 mmol) at −25°. The white viscous product was diluted with diethyl ether (25 cm^3), warmed to room temperature, and left for 24 h. Removal of solvent under reduced pressure yielded a viscous residue which slowly solidified on standing. Distillation then gave 1-phenylvinyl diphenylphosphinate[19] (1.4 g, 30%) (Found: C, 75.3; H, 5.4. Calc for $C_{20}H_{17}O_2P$: C, 75.0; H, 5.4%), b.p. 190–194° at 0.1 mmHg, m.p. 77–78°, δ_P ($CDCl_3$) + 29.7 ppm, δ_H ($CDCl_3$) 5.15 (CH_2=C, m, 2H), 7.2–8.2 (Ar, m, 15H), *m/z* 320 (27%, M^+), 201 (100%), IR (KBr disc) $\nu_{C=C}$ 1622, $\nu_{P=O}$ 1225, ν_{POC} 1029, 1005, 990 cm^{-1}.

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[14]Although S_N2-type cleavage of the alkyl–oxygen bond occurs, reactions of this type follow first-order kinetics in chloroform in accord with rate-determining collapse of the phosphonium-halide ion-pair (Ref. 1).
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