Quasiphosphonium Intermediates. Part I. Preparation, Structure, and Nuclear Magnetic Resonance Spectroscopy of Triphenyl and Trineopentyl Phosphite–Alkyl Halide Adducts

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Experimental conditions for the preparation of triphenyl phosphite–alkyl halide adducts have been investigated. The long periods of heating necessary for reaction of the higher alkyl halides, especially the chlorides and bromides, leads to decomposition with the formation of halogenobenzenes and diphenyl alkylphosphonates, together in certain cases with halogenophosphites, dihalogenophosphites, and other phosphorus-containing compounds. At room temperature, trineopentyl phosphite reacts readily with iodomethane or bromomethane to afford crystalline Michaelis–Arbuzov intermediates, which decompose in solution to yield neopentyl halides without rearrangement of the alkyl group. ^{31}P N.m.r. spectroscopy shows the adducts to have the phosphonium structure $[(RO)_3PR']^+X^-$ (R = Ph or neopentyl), the chemical shifts lying in the range −40 to −50 p.p.m. from 85% H_3PO_4 and being independent of the nature of X (Cl, Br, or I). Molecular weight and conductivity measurements, together with the results of a study of the kinetics of decomposition for trineopentyl phosphite–methyl iodide, are consistent with the presence of ion pairs rather than dissociated ions in chloroform. ^{1}H and ^{31}P N.m.r. chemical shifts occur at slightly lower field for the phosphonium intermediates than for the corresponding diaryl (or dialkyl) alkylphosphonates. Long-range coupling between phosphorus and the α-, β-, and γ-protons is observed, that between phosphorus and the β-protons being greatest.

ALTHOUGH a number of crystalline addition compounds of triaryl phosphites and alkyl halides have been known for a considerable time,[1] their structures have remained uncertain. They have been referred to as ' quasi-phosphonium salts,' the P–X bond being said to be partially ionic and partially covalent in character.[2] Similar compounds have been assumed to occur as intermediates in the reactions of trialkyl phosphites with alkyl halides (Scheme), although until recently the

$$(RO)_3P + R'X \longrightarrow [(RO)_3PR'X] \longrightarrow RX + (RO)_2P(O)R'$$

SCHEME

evidence for their existence was only indirect, being based on changes in refractive index or density,[3] or on thermographic[4] or electrical conductivity measurements,[5] during the course of the Arbuzov reaction. It has recently been shown, however, that crystalline intermediates can be isolated from the sterically hindered trineopentyl phosphite, by virtue of the relatively slow dealkylation by halide ion in the second stage.[6]

Few n.m.r. data have previously been published for adducts of this type but those that are available, viz. for (PhO)$_3$PMeI,[7-9] (PhO)$_3$PMeBr,[9] and certain phosphonite derivatives,[10] suggest a phosphonium structure.[11] We have prepared twenty such derivatives from triphenyl phosphite, two from trineopentyl phosphite, and recorded their ^{31}P spectra. ^{1}H N.m.r. data are also reported for those which were separated as pure products from reaction mixtures. In certain selected cases,

molecular weight and conductivity measurements have been made in order to distinguish amongst structures (1)—(3), which must be considered possible for compounds of this type.

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(1) \qquad (2) \qquad (3)
$$

The preparations of (PhO)$_3$PMeI [1,2] and (PhO)$_3$PEtI [12] have previously been reported and presented no difficulties. However, with increasing bulkiness of the alkyl group, and with decreasing reactivity of the alkyl halides in the order I > Br > Cl, prolonged heating at temperatures up to 200° became necessary and led to further decomposition and side reactions (Table 1). In these sealed-tube reactions of triphenyl phosphite with an alkyl halide the Michaelis–Arbuzov intermediate was in each case identified by its ^{31}P n.m.r. spectrum but isolation as a crystalline solid was not possible if decomposition had occurred to a substantial extent. It was however shown that the chemical shifts were not affected significantly by the presence of other products.

Trialkyl phosphites react relatively rapidly with iodomethane at room temperature, in accord with the greater nucleophilicity of phosphorus in these esters. In the n.m.r. spectrometer at 33·5 °C, reactions of the trialkyl phosphites (RO)$_3$P (R = Me, Et, Pr^i, Bu^n, or

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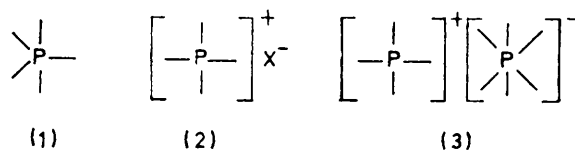[2] S. R. Landauer and H. N. Rydon, Chem. and Ind., 1951, 313; J. Chem. Soc., 1953, 2224.

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TABLE 1

Reactions of triphenyl phosphite [a] with alkyl halides

RX	mol. equiv.	Temp. (°C)	Time (h)	$(PhO)_3PRX$	$(PhO)_3P$	$(PhO)_3PO$ [c]	$(PhO)_2P(O)R$ [d]	$(PhO)_2PX$ [e]	$PhOPX_2$ [e]	Unidentified [f]
MeI	1·40	100	11	98		2				
MeBr [g]	1·10	100	50	90 [h,i]						
MeCl	3·20	100—135	872	78 [h,i]						
EtI	1·33	100	230	98		2				
EtBr	1·27	125	470	89 [h,k]						
EtCl	1·21	178	890	10	25	5	55	5		
Pr^{n}I	1·33	100	1,000	90 [l]		3	7			
Pr^{n}Br	1·25	135—140	1,150	55	25	7	10	3		
Pr^{n}Cl	1·26	170—180	1,115	7	40	3	30	20		
Pr^{i}I	1·28	140	380	97		3				
Pr^{i}Br	1·33	140—175	538	40		20	20			20 (−10 p.p.m.)
Pr^{i}Cl	1·49	[m] {170—175	538	5						
		180—200	980	0	40	3	45	12		
Bu^{n}I	1·34	155	360	65	15	5	15			
Bu^{n}Br	1·51	155	390	35	20	10	30	5		
Bu^{n}Cl	1·57	183	320	20	30	3	40	7		
Bu^{i}I	1·24	155	400	60	25	7	5			3 (+25 p.p.m.)
Bu^{i}Br	1·52	155	360	15	7	15	15	15	18	15 (+25 p.p.m.)
Bu^{i}Cl	1·65	[m] { 183	320	10						
		190—205	660	0	20	5	15	45	15	
Bu^{t}Br	1·46	150	140	0	50	15		25	7	3 (+25 p.p.m.)
Bu^{t}Cl	1·72	150	140	0	40	3		30	7	20 (−30 p.p.m.)
PhCH$_2$Br	1·36	150 [n]	168	40		25	30			5 (+25 p.p.m.)
PhCH$_2$Cl	1·44	150	310	50	10	5	20			10 (−76 p.p.m.)

[a] ca. 2 g in sealed n.m.r. tubes unless otherwise specified. [b] By integration of characteristic peaks,[11] except where yield of isolated product is given. [c] From oxidation by atmospheric O_2. [d] Arbuzov reaction product. [e] Probably from hydrogen halide (resulting by elimination from RX) thus: $(PhO)_3P + HX \rightleftharpoons (PhO)_2PX + PhOH$; $(PhO)_2PX + HX \rightleftharpoons PhOPX_2 + PhOH$ (H. R. Hudson and J. C. Roberts, unpublished work). [f] Assuming one P atom per molecule. [g] $(PhO)_3P$ (14·4 g) and MeBr (4·5 g). [h] Isolated as white crystalline solids by washing with anhydrous ether. [i] Found: C, 56·5; H, 4·6; P, 7·4. Calc. for $C_{19}H_{18}BrO_3P$: C, 56·3; H, 4·5; P, 7·6%; m.p. (sealed tube) 152°. [j] Methyltriphenoxyphosphonium chloride (Found: C, 62·6; H, 5·4; Cl, 9·3. $C_{19}H_{18}ClO_3P$ requires C, 63·3; H, 5·0; Cl, 9·8%), m.p. (sealed tube) 123°. [k] Ethyltriphenoxyphosphonium bromide (Found: C, 57·1; H, 5·1; Br, 18·8; P, 7·0. $C_{20}H_{20}BrO_3P$ requires C, 57·3; H, 4·8; Br, 19·1; P, 7·4%), m.p. (sealed tube) 52°. [l] A similar experiment at 140° (390 h) yielded n-propyltriphenoxyphosphonium iodide (93%) as a viscous brown liquid (Found: C, 49·0; H, 4·7; I, 25·9; P, 6·0. $C_{21}H_{22}IO_3P$ requires C, 52·5; H, 4·6; I, 26·4; P, 6·5%) after washing with ether. The product could not be crystallized. [m] Successive periods of heating for the same sample. [n] Reaction at 170° led to other unidentified by-products (−10 and −149 p.p.m.).

TABLE 2

^{31}P N.m.r. chemical shifts for Michaelis–Arbuzov intermediates [a] and corresponding phosphonates [b]

	Intermediates				Phosphonates	
		δ [c]				
Compound	X = Cl	X = Br	X = I	Compound	δ [c]	
$(PhO)_3PMeX$	−41 (q)	−41 (q)	−41 (q)	$(PhO)_2P(O)Me$	−24 (q)	
$(PhO)_3PEtX$	−40 (m)	−40 (m)	−40 (m)	$(PhO)_2P(O)Et$	−26·5 (m)	
$(PhO)_3PPr^nX$	−38 (m)	−38 (m)	−38 (m)	$(PhO)_2P(O)Pr^n$	−26·5 (m)	
$(PhO)_3PPr^iX$	−38 (m)	−38 (m)	−38 (m)	$(PhO)_2P(O)Pr^i$	−26 (m)	
$(PhO)_3PBu^nX$	−38 (m)	−38 (m)	−38 (m)	$(PhO)_2P(O)Bu^n$	−26·5 (m)	
$(PhO)_3PBu^iX$	−38 (m)	−38 (m)	−38 (m)	$(PhO)_2P(O)Bu^i$	−26 (m)	
$(PhO)_3P(CH_2Ph)X$	−30 (t)	−30 (t)		$(PhO)_2P(O)CH_2Ph$	−19 (t)	
$(Me_3C \cdot CH_2O)_3PMeX$		−54 (m)	−54 (m)	$(Me_3C \cdot CH_2O)_2P(O)Me$	−29·5 (m)	

[a] 45—48% w/v in $CHCl_3$. [b] Neat liquids. [c] From 85% H_3PO_4.

TABLE 3

^1H N.m.r. data for triphenyl phosphite adducts [a] and diphenyl alkylphosphonates [b]

Compound	PhO	CHα	CHβ	CHγ	CHαCHβ	CHβCHγ	PCHα	PCCHβ	PCCCHγ
$(PhO)_3PMeI$	2·55 (m)	6·92 (d)					16·7		
$(PhO)_3PMeBr$	2·55 (m)	6·74 (d)					17·2		
$(PhO)_3PMeCl$	2·55 (m)	6·82 (d)					17·0		
$(PhO)_2P(O)Me$	2·82 (m)	8·32 (d)					17·9		
$(PhO)_3PEtI$	2·55 (m)	6·41 (m) [c]	8·53 (m) [d]		7·8		15·4	24·1	
$(PhO)_3PEtBr$	2·55 (m)	6·36 (m) [c]	8·54 (m) [d]		7·8		15·7	24·8	
$(PhO)_2P(O)Et$	2·82 (m)	8·05 (m) [c]	8·77 (m) [d]		7·5		21·0	25·0	
$(PhO)_3PPr^nI$	2·55 (m)	6·60 (m) [e]	8·10 (m)	8·80 (m) [d]	7·6	6·4	15·4		2·8

[a] 12—14% w/v in $CDCl_3$. [b] 50% v/v in $CDCl_3$. [c] Two overlapping quartets. [d] Two triplets. [e] Two overlapping triplets.

Bu^j) were essentially complete in 5—15 h but in no case did the concentration of the intermediate reach a level detectable by n.m.r. spectroscopy. However, on treatment of the more sterically hindered trineopentyl phosphite with either iodomethane [6] or bromoethane in slight excess, the Arbuzov intermediate slowly crystallized and could be washed with ether to yield colourless crystals, which were sensitive to air or moisture, but which were stable indefinitely under anhydrous ether or

group (Me < Et < higher alkyl) and the consequent increase in electron density on phosphorus. The benzyl group (+I less than for Me) does not however fit this trend and again the anisotropic effect of the additional phenyl group is probably important. Long-range coupling is observed between phosphorus and the α-, β-, and γ-protons in both the phosphonium ions and the phosphonates. Coupling to the β-protons is greatest, in both series. Although no simple explanation of this

TABLE 4

^{1}H N.m.r. data for trineopentyl phosphite adducts [a] and dineopentyl methylphosphonate [b]

Compound	τ			Coupling constants (Hz)	
	Me$_3$C	MeP	CH$_2$O	PCH	POCH
(Me$_3$C·CH$_2$O)$_3$PMeI	8·96 (s)	7·27 (d)	5·69 (d)	16·75	4·9
(Me$_3$C·CH$_2$O)$_3$PMeBr	8·96 (s)	7·19 (d)	5·69 (d)	17·0	5·0
(Me$_3$C·CH$_2$O)$_2$P(O)Me	9·05 (s)	8·55 (d)	6·34, 6·27 [c]	17·65	5·4

[a] 11% w/v in CDCl$_3$. [b] 33% v/v in CDCl$_3$; 100 MHz spectrum. [c] AB of ABX spectrum, J_{AB} 9·4, $J_{POCH_A} = J_{POCH_B} = 5·4$ Hz. Magnetic non-equivalence attributed to attachment (via oxygen) to asymmetric P (M. P. Williamson and C. E. Griffin, J. Phys. Chem., 1968, 72. 4043).

in a desiccator. Transient crystals have also been observed in the reaction of tri-t-butyl phosphite with iodomethane but were not isolated.[13]

It is clear from the ^{31}P n.m.r. data (Table 2) that in chloroform solution the intermediates have the simple phosphonium structure (2). ^{31}P Chemical shifts lie in the range —38 to —41 p.p.m. (R = Ph) or at —54 p.p.m. (R = Me$_3$C·CH$_2$) and are independent of the nature of X. Similar values have been reported for methyltriphenoxyphosphonium tetrafluoroborate (—38 p.p.m.) [9] and for the alkyltrialkoxyphosphonium hexachloroantimonates (48—54 p.p.m.) [14] and tetrafluoroborates (46—48 p.p.m.).[9] No signals could be detected in the regions characteristic of PX$_6$⁻ or PX$_5$.[11] ^{31}P and ^{1}H Chemical shifts for the phosphonium intermediates occur at lower field than do the corresponding shifts for the phosphonates which they yield on decomposition (Tables 2—4). These differences are probably associated with greater p_π–d_π bonding between oxygen and phosphorus in the phosphonates and are analogous to those reported between the alkoxyphosphonium hexachloroantimonates and the corresponding phosphoryl compounds.[14] On a similar basis one might expect the trineopentyl phosphite adducts to have chemical shifts at higher field than those for the triphenoxy-compounds because of mesomeric interaction of the oxygen lone pairs with the benzene rings in the latter. The reverse is in fact observed for the phosphorus resonances. As with the parent phosphites,[11] the phenoxy-derivatives have ^{31}P chemical shifts at higher field and it is likely that the anisotropic effect of the phenyl rings is an important factor. Within the alkyltriphenoxyphosphonium halide series, a slight upfield shift (from —41 to —38 p.p.m.) can be correlated with increasing inductive electron release by the alkyl

can be given, similar observations have been reported elsewhere.[15] Attempts to record the ^{31}P n.m.r. spectra of the intermediates in the solid state were unsuccessful but by analogy with related compounds [16] it is likely that they form ionic crystals. Their insolubility in ether supports this view.

Conductivity and molecular weight measurements indicate that the compounds exist as ion pairs in chloroform solution. Thus triphenyl phosphite–methyl iodide and –ethyl iodide had molecular weights which corresponded to the undissociated monomers, and the conductivity of the methyl iodide adduct was low (Table 5).

TABLE 5

Equivalent conductances of phosphonium halides

Compound	Solvent	Conc. (g. equiv. l⁻¹)	Λ/ohm⁻¹ cm²
Ph$_3$PMeI	CHCl$_3$	0·0866	2·64
Ph$_3$PMeI	CH$_3$CN	0·0846	90·16
(PhO)$_3$PMeI	CHCl$_3$	0·1028	0·994
(PhO)$_3$PMeI	CH$_3$CN	0·1055	48·5

In acetonitrile an increase in conductivity indicated some dissociation, although less than for the analogous Ph$_3$MePI, for which the conductance in this medium approached a value which might be expected for a 1 : 1 electrolyte.[17,18]

The first-order kinetics which have been noted in the decomposition of trineopentyl phosphite–methyl iodide in chloroform [6] are also consistent with a low steady-state concentration of dissociated ions in this medium: [(RO)$_3$P⁺Me]I⁻ ⇌ (RO)$_3$P⁺Me + I⁻ ⟶ RI + (RO)$_2$P(O)Me. Absence of alkyl rearrangement and of elimination indicates that the second step is exclusively an S_N2 process. Results for the interaction of cis- and

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trans-2-ethoxy- and 2-isopropoxy-4-methyl-1,3,2-dioxa-phosphorinan with alkyl iodides have shown a lack of stereospecificity at phosphorus which appears to require the intervention of a five-co-ordinate Arbuzov intermediate.[19] We did not find that such an intermediate reached a spectroscopically detectable level in the present work, although it could have been formed as a short-lived species en route to the phosphonium structure.

EXPERIMENTAL

Materials.—Triphenyl phosphite and the alkyl halides were obtained commercially and redistilled before use. Trineopentyl phosphite, b.p. 82—83° at 0·25 mmHg, m.p. 54—55°, δ_P −138 p.p.m. (septet), τ (CDCl$_3$) 9·09 (Me$_3$C, s) and 6·57 (CH$_2$, d, J_{POCH} 6·55 Hz), was obtained in 91% yield from the alcohol (29·4 g), phosphorus trichloride (15·3 g), and dimethylaniline (40·4 g) in petroleum (b.p. 30—40°), by a standard procedure.[20] Traces of dimethyl-anilinium chloride were finally removed by dissolving the product in anhydrous diethyl ether, filtering, and evaporating.

N.m.r. Spectroscopy.—N.m.r. spectra were recorded on a Perkin-Elmer R10 spectrometer operating at 60 MHz with Me$_4$Si as internal standard for ^{1}H spectra or at 24·3 MHz with 85% H$_3$PO$_4$ as external standard for ^{31}P spectra. 100 MHz ^{1}H N.m.r. data for dineopentyl methylphosphonate were recorded at the P.C.M.U. (Harwell).

Molecular Weight Determinations.—Molecular weights in anhydrous chloroform (dried; P$_2$O$_5$) were determined with a Gallenkamp semi-micro ebulliometer against benzil (M 210·23) as standard.

Conductances.—Measurements were made at 25° with a Jones cell [17] and a Wayne–Kerr bridge, and results are reported in Table 5. Values remained constant for several hours.

Triphenyl Phosphite Adducts.—Methyltriphenoxyphos-phonium iodide, m.p. (sealed tube) 114°, M (in CHCl$_3$) 475, 478 (Calc. for C$_{19}$H$_{18}$IO$_3$P: M, 452), and ethyltriphenoxy-phosphonium iodide, m.p. (sealed tube) 88—90°, M (in CHCl$_3$) 467, 453 (Calc. for C$_{20}$H$_{20}$IO$_3$P: M, 466), were prepared as described previously.[1,2,12] Other derivatives of triphenyl phosphite were prepared by heating the phosphite with the appropriate alkyl halide in a sealed tube as specified in Table 1, the reactions being monitored periodically by ^{31}P n.m.r.

Trineopentyl Phosphite Adducts.—Trineopentyl phosphite (2·7 g) and iodomethane (1·6 g, 1·2 mol. equiv.) were mixed

[19] C. L. Bodkin and P. Simpson, *Chem. Comm.*, 1970, 1579; *J.C.S. Perkin II*, 1972, 2049.

and left at room temperature (8 h). The white crystals which separated were washed with anhydrous ether to yield *methyltrisneopentyloxyphosphonium iodide* (1·8 g, 46%), m.p. (sealed tube) 86° (Found: C, 44·3; H, 8·5; I, 28·8; P, 6·9. C$_{16}$H$_{36}$IO$_3$P requires C, 44·3; H, 8·4; I, 29·2; P, 7·1%). With a larger quantity of iodomethane (2·43 mol. equiv.) in an n.m.r. tube at 33·5°, no crystals separated; after 2 h the tube contained (R = Me$_3$C·CH$_2$): (RO)$_3$P (30%), (RO)$_3$PMeI (30%), and (RO)$_2$P(O)Me (40%); after 8 h only the phosphonate was detectable.

Similarly, trineopentyl phosphite (2·1 g) and bromo-methane (0·9 g, 1·3 mol. equiv.) at room temperature (48 h) gave *methyltrisneopentyloxyphosphonium bromide* (1·2 g, 42%), m.p. (sealed tube) 87° (Found: C, 49·7; H, 9·5; Br, 20·3; P, 7·6. C$_{16}$H$_{36}$BrO$_3$P requires C, 49·6; H, 9·4; Br, 20·6; P, 8·0%).

Phosphonates.—Hydrolysis of the corresponding triphenyl phosphite–alkyl halide adducts (*ca.* 15 g) with 2M-NaOH at room temperature, followed by separation and drying (Na$_2$SO$_4$) of the oily layer gave: (i) diphenyl methyl-phosphonate (87%) (Found: P, 12·2. Calc. for C$_{13}$H$_{13}$O$_3$P: P, 12·5%), m.p. 35°; (ii) diphenyl ethylphosphonate (91%) (Found: P, 11·5. Calc. for C$_{14}$H$_{15}$O$_3$P: P, 11·8%), b.p. 131—132° at 0·15 mmHg, n_D^{20} 1·5470. Other diphenyl alkylphosphonates were identified in reaction products by ^{31}P n.m.r.

Trineopentyl phosphite (10·6 g) and iodomethane (9·4 g, 1·83 mol. equiv.) were heated under reflux (90°; 20 h). Distillation gave dineopentyl methylphosphonate (6·9 g, 81%), b.p. 61—63° at 0·2 mmHg, n_D^{20} 1·4229 (Found: P, 12·8. Calc. for C$_{11}$H$_{25}$O$_3$P: P, 13·1%).

Decomposition of Methyltrisneopentyloxyphosphonium Iodide in Chloroform.—The iodide (0·5475 g) in anhydrous chloroform (made up to 5 ml at 34°) was placed in the n.m.r. spectrometer (33·5°) and its rate of decomposition measured by following the disappearance of the methylene ^{1}H doublet. Excellent first-order kinetics (k_1 1·1 × 10^{-4} s^{-1}) were observed up to at least 85% completion. Neo-pentyl iodide [τ 8·95 (Me$_3$C, s) and 6·85 (CH$_2$, s)] was formed. t-Pentyl iodide and olefins were not detectable. The bromide likewise decomposed without alkyl re-arrangement.

[20] W. Gerrard and H. R. Hudson, ' Organic Derivatives of Phosphorous and Thiophosphorous Acid,' in ' Organic Compounds of Phosphorus,' eds. G. M. Kosolopoff and L. Maier, Wiley, New York, 1973, vol. 5, ch. 13, p. 32.