Memory Effects and Site Selectivity in the β-Scission of Tetra-alkoxyphosphoranyl Radicals

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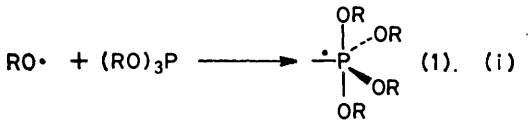
Cyclic and acyclic phosphoranyl radicals of the type $(RO)_2\dot{P}(OR^1)OR^2$ have been generated by both the reactions $(RO)_2POR^1 + R^2O\cdot$ and $(RO)_2POR^2 + R^1O\cdot$ and shown to undergo β-scission to give $R^{1}\cdot$ and $R^{2}\cdot$, such that the relative yields of these alkyl radicals are independent of the source of the phosphoranyl intermediate. The phosphoranyl radical exhibits no ' memory ' of its origin. E.s.r. line-shape effects and the results of ^{13}C-labelling studies are interpreted in terms of rapid exchange of apical and equatorial alkoxy ligands in $(RO)_4P\cdot$. It is concluded that, in general, the high rate of alkoxy ligand exchange in the phosphoranyl intermediate will preclude the detection of a memory effect in phosphite oxidation by alkoxyl radicals. Both the formation [from RO· and $(RO)_3P$] and the β-scission of $(RO)_4P\cdot$ appear to be site-selective processes. The entering alkoxyl radical becomes an apical ligand and cleavage of a C–O bond occurs more readily in an apical alkoxy group. A scheme is presented to account for these site selectivities and for the mobility of the ligands in phosphoranyl radicals. It is suggested that a species in which the unpaired electron is confined to one σ*-P–ligand orbital is a common intermediate in these processes.

ALKOXYL radicals add rapidly to trialkyl phosphites to form tetra-alkoxyphosphoranyl radicals (1) which may



(1). (i)

(1) $\xrightarrow{\beta\text{-Scission}}$ $(RO)_3P{=}O + R\cdot$ (ii)

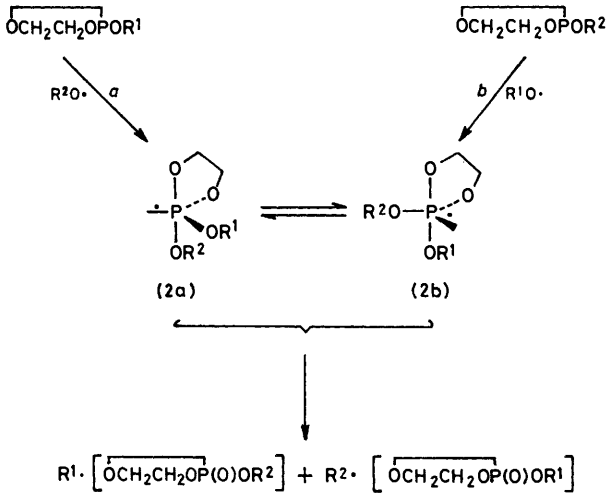
undergo subsequent β-scission to yield phosphate and an alkyl radical [equations (i) and (ii)].[1-3]

Since the apical and equatorial ligands in (1) are non-equivalent, the β-scission of the phosphoranyl radical may be *site-selective*, that is the alkyl radical may be formed at different rates from apical and equatorial alkoxy groups. The attack of the alkoxyl radical on the phosphite is probably also site-selective, with the incoming group taking up an apical ligand site in (1).[4,5] These site-selectivities could give rise to a *memory effect* in experiments of the type shown in Scheme 1, provided that apical–equatorial ligand exchange interconverting

[1] A. G. Davies, D. Griller, and B. P. Roberts, *J.C.S. Perkin II*, 1972, 993, 2224.
[2] G. B. Watts, D. Griller, and K. U. Ingold, *J. Amer. Chem. Soc.*, 1972, **94**, 8784.
[3] W. G. Bentrude in ' Free Radicals,' ed. J. K. Kochi, Wiley, New York, 1973, vol. II, ch. 22.
[4] J. W. Cooper and B. P. Roberts, *J.C.S. Chem. Comm.*, 1977, 228.
[5] W. G. Bentrude and T. B. Min, *J. Amer. Chem. Soc.*, 1972, **94**, 1025; 1976, **98**, 2918.

(2a and b) is *slower* than β-scission. The final products from routes *a* and *b* could be different; because the phosphoranyl radical (2) can exist in two isomeric forms it may have a ' memory ' of its origin.

Bentrude and Min [5] have detected memory effects in reactions of alkoxyl radicals with certain acyclic phosphites and interpreted their results in terms of apical site-selectivity in β-scission. We have reported preliminary results which demonstrate the absence of a



SCHEME 1

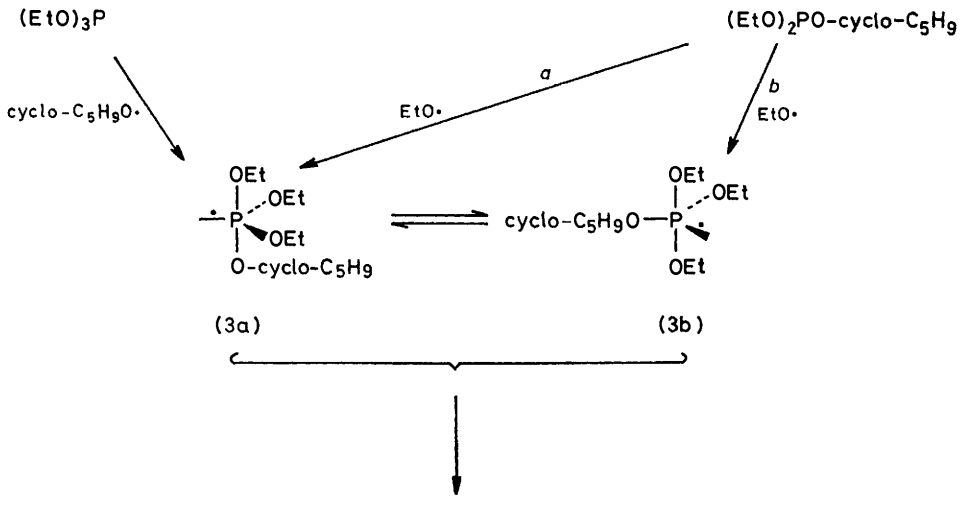
memory effect for the system shown in Scheme 1 (R^1 = Bu^t, R^2 = Pe^t).[6] We have concluded [6] that it should not, in general, be possible to detect memory effects since, at least when $R^{1}\cdot$ and $R^{2}\cdot$ are unstabilised alkyl radicals, β-scission will not be sufficiently rapid to compete with apical–equatorial ligand exchange.

In this paper we report in full our attempts to detect memory effects in homolytic phosphite oxidation and experiments designed to investigate site-selectivity in the β-scission of and ligand exchange in tetra-alkoxyphosphoranyl radicals.

RESULTS AND DISCUSSION

(a) *Memory Effects.*—Mixtures of a trialkyl phosphite and a dialkyl peroxide (as a photochemical source of alkoxyl radicals) were irradiated with u.v. light whilst in the cavity of an e.s.r. spectrometer, and the spectra of the phosphoranyl and alkyl radicals produced were recorded during continuous photolysis. Two systems of the type shown in Scheme 1 and one pair of experiments with acyclic phosphites (see Scheme 2 which assumes apical entry of the alkoxyl radicals) were investigated.

The advantage of using a dioxaphospholan (Scheme 1) is that the five-membered ring has a strong preference to bridge apical and equatorial sites in the intermediate phosphoranyl radicals,[7,8] and thus, provided that the alkoxyl radical enters site-specifically, one pair of reagents should lead to only one isomer of the phosphoranyl radical. In the acyclic system (Scheme 2) the rate of reaction *b* should be about twice that of *a* (the statistical factor), since the reactions are very fast [1] (and hence not likely to be selective) and the apicophilicities of ethoxy and cyclopentoxy groups are expected to be similar.[8] The ratio of the concentrations of alkyl radicals was measured at relatively high temperatures when the concentrations of phosphoranyl radicals were negligible. The ratio of alkyl radical concentrations was independent of light intensity (I), whilst the individual concentrations were proportional to $I^{0.5}$ and any residual phosphoranyl radical concentration was proportional to $I^{1.0}$. The results are gathered in Table 1.



SCHEME 2

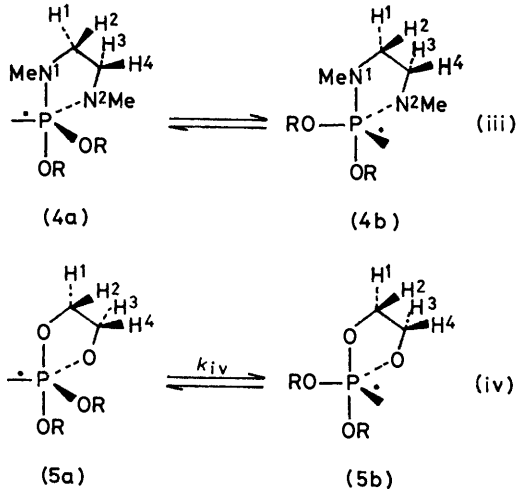
Clearly none of the three systems studied exhibits a memory effect. System B was examined since it appeared feasible that the extra bulk of the Pr^{i}Me$_2$CO group might alter the rates of β-scission and ligand

[6] M. J. Parrott and B. P. Roberts, *J. Organometallic Chem.*, 1975, **99**, C49.

[7] R. W. Dennis and B. P. Roberts, *J.C.S. Perkin II*, 1975, 140.

[8] J. W. Cooper, M. J. Parrott, and B. P. Roberts, *J.C.S. Perkin II*, 1977, 730.

exchange to a point where a memory effect might be detected. β-Scission could be more site-selective for cleavage of primary and secondary alkyl–oxygen bonds compared with the weaker tertiary alkyl–oxygen bond. An attempt to detect a memory effect for $\overset{\frown}{OCH_2CH_2OP}$-(OEt)O-cyclo-$C_5H_9$ failed, since ring-opening β-scission to give $\cdot CH_2CH_2OP(O)(OEt)O\text{-cyclo-}C_5H_9$ [$a(2H_\alpha)$ 22.4, $a(2H_\beta)$ 27.2 G at 290 K] was the major fragmentation process, and the concentrations of Et· and cyclo-C_5H_9· were too small to measure. However, the analogous acyclic system C showed no memory effect.*



The absence of a memory effect in these systems may be due to one or more of the following reasons: (1) phosphoranyl radical formation is not detectably site-selective; (2) β-scission is not detectably site-selective; (3) apical–equatorial ligand exchange is rapid compared with β-scission.

(b) *Ligand Exchange in Phosphoranyl Radicals.*—Many examples are now known of phosphoranyl radicals which undergo intramolecular ligand exchange at rates sufficiently large as to give rise to line-shape effects in their e.s.r. spectra. The rate constants for exchange of apical and equatorial H,[8,10] F,[11] R_2N,[7] and CH_3 [12] ligands in appropriate phosphoranyl radicals are in the range 10^7—10^{10} s^{-1} at *ca.* 273 K. Evidence for rapid exchange of apical and equatorial alkoxy groups is less direct. Line-shape effects observed for the e.s.r. spectrum of (4; R = Bu^t or Et) [7] and the magnetic equivalence of the quasi-apical methyleneoxy ring protons of (5; R = Bu^t or Et) [8] have been attributed to rapid exchange of the exocyclic alkoxy ligands in the M4 mode [13] shown in equations (iii) and (iv).

It is worth recalling at this point that the line-shape changes observed for (4) are as expected for ring-proton exchange *without* simultaneous exchange of N^1 and N^2.[7] Deuterium labelling studies of (5) also show that H^1 exchanges with H^2 and *not* H^3.[8] Hence the M4 mode of ligand exchange is more rapid [at least for (4) and (5)] than the thermodynamically equally favourable M1 mode, which would be the result of Berry pseudorotation with the orbital of the unpaired electron as pivot.

Although only the fast-exchange limiting spectrum could be obtained for (5; R = Bu^t or Et), we have now detected line-shape effects over the whole range of exchange rates for (5; R = Me_3Si), produced by addition of photochemically generated trimethylsiloxyl radicals to (6; X = H) (see Figure 1).

At low temperature the spectrum of (5; R = Me_3Si) exhibits a doublet splitting, ascribed to H^1 in (5a) [or H^2 in (5b)], whereas at high temperatures a triplet is observed as a result of rapid exchange of H^1 in (5a) with another ring proton which itself couples to a negligible extent. When the phosphoranyl radical was generated

$$Me_3SiO_2SiMe_3 \xrightarrow{h\nu} 2Me_3SiO\cdot \qquad (v)$$

$$Me_3SiO\cdot + \overset{\frown}{OCH_2CX_2OP}OSiMe_3 \longrightarrow \overset{\frown}{OCH_2CX_2OP}(OSiMe_3)_2 \qquad (vi)$$

(6)

* Professor Bentrude [9] has informed us that, on use of different alkoxyl radical sources, some of the systems [5] for which he previously reported a memory effect now fail to show one.

[9] W. G. Bentrude, personal communication.

[10] P. J. Krusic and P. Meakin, *Chem. Phys. Letters*, 1973, **18**, 347.

[11] I. H. Elson, M. J. Parrott, and B. P. Roberts, *J.C.S. Chem. Comm.*, 1975, 586.

[12] J. W. Cooper and B. P. Roberts, *J.C.S. Perkin II*, 1976, 808.

[13] J. I. Musher, *J. Chem. Educ.*, 1974, **51**, 94.

TABLE 1

Attempts to detect memory effects in homolytic phosphite oxidation

System	Phosphite [a]	Peroxide [a]	T/K	Alkyl radical concentration ratio
A	$\overset{\frown}{OCH_2CH_2OP}OBu^t$	Pe^tOOPe^t	253	$[Pe^t\cdot] : [Bu^t\cdot]$ 1.21 ± 0.03
A	$\overset{\frown}{OCH_2CH_2OP}OPe^t$	Bu^tOOBu^t	253	$[Pe^t\cdot] : [Bu^t\cdot]$ 1.23 ± 0.03
B	$\overset{\frown}{OCH_2CH_2OP}OBu^t$	$Pr^iMe_2COOCMe_2Pr^i$	251	$[Pr^iMe_2C\cdot] : [Bu^t\cdot]$ 2.48 ± 0.05 [b]
B	$\overset{\frown}{OCH_2CH_2OP}OCMe_2Pr^i$	Bu^tOOBu^t	251	$[Pr^iMe_2C\cdot] : [Bu^t\cdot]$ 2.52 ± 0.05
C	$(EtO)_3P$	cyclo-C_5H_9OO-cyclo-C_5H_9	293	$[C_5H_9] : [Et\cdot]$ 1.07 ± 0.05
C	$(EtO)_2PO$-cyclo-C_5H_9	EtOOEt	293	$[C_5H_9\cdot] : [Et\cdot]$ 1.10 ± 0.05

[a] Cyclopropane solvent; Pe^t = t-pentyl. [b] The spectrum of the isopropyl radical was also detected in this experiment. This species is formed by β-scission of $Pr^iMe_2CO\cdot$, which is competitive with addition of the alkoxyl radical to the phosphite.

from (6; X = D) the spectra (see Figure 1) indicated [8] that exchange of H with H, and not H with D, occurred.

Hence the line-shape effects detected for (5; R = Me_3Si) are consistent with the M4(exocyclic) exchange [8] shown in equation (iv), and not with the M1 mode resulting from Berry pseudorotation with the unpaired electron as pivot. The rate constant k_{iv} (R = Me_3Si) is

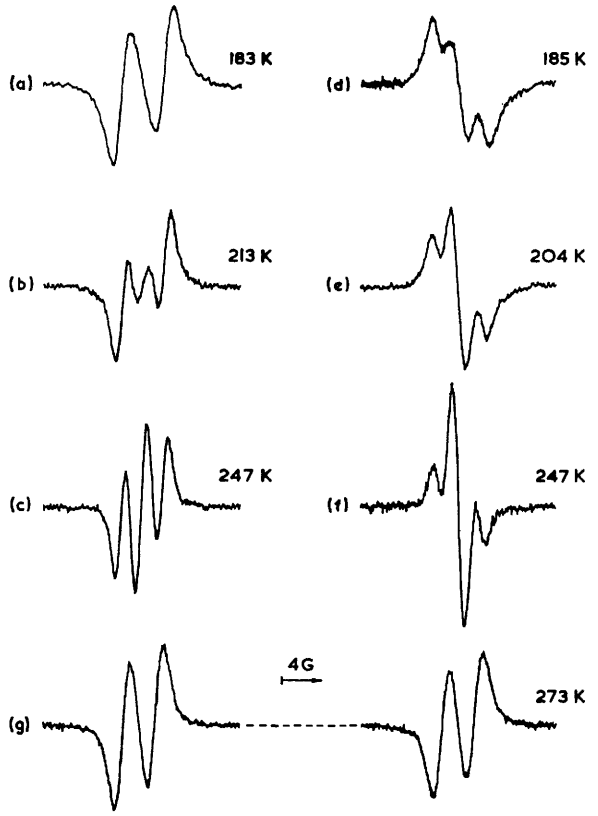


FIGURE 1 E.s.r. spectra of phosphoranyl radicals in cyclopropane solution at the temperatures indicated: (a)—(c) $\overline{OCH_2CH_2O\dot{P}}$-$(OSiMe_3)_2$ (m_I ^{31}P $+\frac{1}{2}$ transitions only); (d)—(f) $\overline{OCH_2CD_2O\dot{P}}$-$(OSiMe_3)_2$ (m_I ^{31}P $+\frac{1}{2}$ transitions only); (g) $\overline{OCH_2CH_2O\dot{P}}$-$(OSiMe_3)OBu^t$

appreciably less than k_{iv} (R = Bu^t or Et) at the same temperature. Computer simulation of the spectra in the range 190—147 K [taking $a(H^1)$ 4.1, $a(H^2)$ 0.1 G in (5a)] gave log $(k_{iv}/s^{-1}) = 12.7 - 20.5/\theta$, where $\theta = 2.303RT$ kJ mol^{-1}. At 273 K for (5; R = Bu^t or Et) we have estimated [8] that k_{iv} is $\geqslant 6 \times 10^9$ s^{-1}, whereas the extrapolated value for (5; R = Me_3Si) is 6×10^8 s^{-1}.

In an attempt to obtain more direct evidence of alkoxy ligand exchange, we have generated a number of phosphoranyl radicals containing the $^{13}CH_3O$ group and examined the ^{13}C splitting from this ligand. The radicals were produced by photolysis of ^{13}C-labelled (96 atom %) dimethyl sulphoxylate [14] [equation (vii; Me* = $^{13}CH_3$)] in the presence of the appropriate phosphite.

* The linewidth was the same for $(CD_3O)_4P\cdot$ [generated by photolysis of $(CD_3O)_2S$ in the presence of $(CD_3O)_3P$] under identical conditions and is thus not determined by unresolved proton splittings.

The spectrum of the tetramethoxyphosphoranyl radical, $(MeO)_4P\cdot$, generated in cyclopropane from unlabelled $(MeO)_3P$ and $(MeO)_2S$, showed a peak–peak linewidth of 0.5 G at 213 K and no splitting other than that

$$Me^*OSOMe^* \xrightarrow{h\nu} Me^*O\cdot + \cdot SOMe^* \quad \text{(vii)}$$

from ^{31}P.* Under similar conditions radical (7) gave rise to a single e.s.r. spectrum which showed a splitting of 1.0 G from one ^{13}C nucleus. Radical (8), generated from

$(MeO)_3\dot{P}OMe^*$ (7) $\qquad$ $(Me^*O)_3\dot{P}OMe$ (8)

$\overline{OCH_2CH_2O\dot{P}}(OR^1)OR^2$ (9)

labelled phosphite, showed splitting (1.0 G) from *three apparently equivalent* ^{13}C nuclei, although (8) must contain both apical and equatorial labelled methoxy groups. These results imply that apical and equatorial Me*O groups give rise to very similar ^{13}C splittings and/or that exchange of these labelled ligands is rapid on the e.s.r. time scale.

The spectra of radicals (9; R^1, R^2 = Me, Me*) are shown in Figure 2. The spectrum of the radical (9; $R^1 = R^2$ = Me) shows splitting from two ring protons, whilst the spectrum of (9; $R^1 = R^2$ = Me*) shows additional splitting (0.9 G) from two *apparently equivalent* ^{13}C nuclei. Since (9; $R^1 = R^2$ = Me*) presumably contains both apical and equatorial Me*O groups, this result again implies that these ligands give rise to similar splittings or that they are exchanging rapidly. An

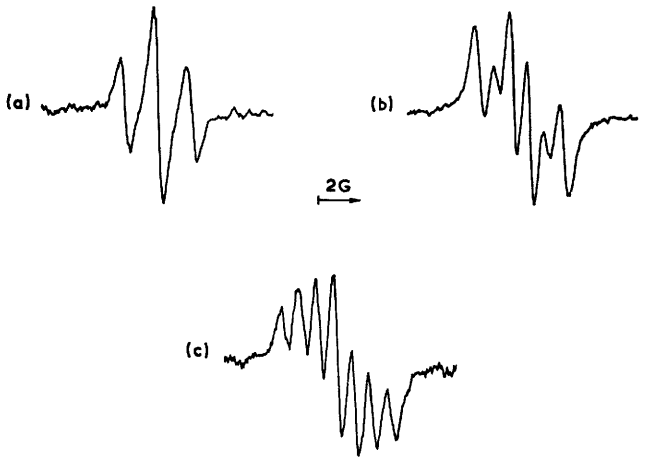


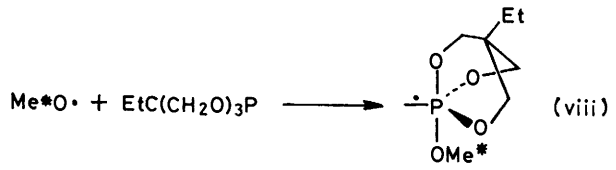
FIGURE 2 E.s.r. spectra of the phosphoranyl radicals (9) in cyclopropane at 253 K: (a) $\overline{OCH_2CH_2O\dot{P}}(OMe)_2$; (b) $\overline{OCH_2CH_2O\dot{P}}(OMe^*)OMe$; (c) $\overline{OCH_2CH_2O\dot{P}}(OMe^*)_2$. Only the low field ($m_I$ ^{31}P $+\frac{1}{2}$) transitions are shown

identical spectrum was obtained for the radical (9; R^1 = Me, R^2 = Me*) whether it was generated from labelled sulphoxylate and unlabelled phosphite or *vice*

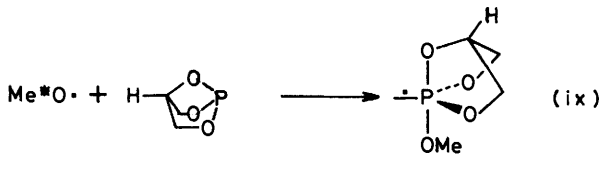
[14] J. S. Chapman, J. W. Cooper, and B. P. Roberts, *J.C.S. Chem. Comm.*, 1976, 835.

versa. From either source a doublet splitting (0.9 G) from one ^{13}C nucleus was observed.

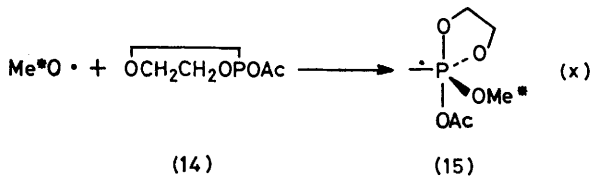
Addition of Me*O to (10) or (11) gave the phosphoranyl radicals (12) or (13), respectively, both of which presumably possess apical Me*O groups, although these caged radicals possibly have structures somewhat different from those of their acyclic and monocyclic analogues.



(10) (12)



(11) (13)



(14) (15)

The ^{13}C splittings for (12) and (13) were 4.5 (263 K) and 3.5 G (253 K), respectively.

Addition of Me*O· to (14) gave a spectrum which did not show resolvable ^{13}C splitting and which was indistinguishable from that of the unlabelled radical. The apicophilicities of the acetoxy and methoxy groups are certainly different and that of AcO is probably appreciably greater,[8] forcing the Me*O group into an equatorial site in the radical (15).

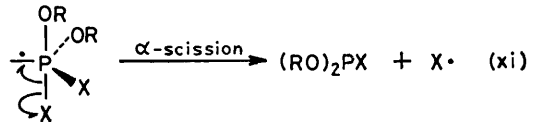
However, the peak–peak linewidth for the spectrum of (15) was 1.6 G and thus the splitting from the equatorial methoxy carbon *may* be as large as *ca.* 0.8 G. Similar results were obtained by addition of MeO· and Me*O· to $\overline{OCH_2CH_2OPOSiMe_3}$, but here the linewidth was even greater. Whilst these experiments are not unambiguous, they do tend to show that the magnitude of $a(^{13}C)$ will be greater for an apical Me*O group than for one situated equatorially. Hence we conclude that rapid exchange of methoxy ligands in (8) and (9; $R^1 = R^2 = Me^*$) is probably responsible for the apparent equivalence of the Me*O groups. A conservative estimate of the rate constant for exchange would be $\geqslant 10^8$ s^{-1} at 273 K, as expected, since the M4 process shown in equation (iv; R = Me, Me*) requires that exchange of the methoxy ligands and of the ring protons H^1 and H^2 occurs at the same rate. The observed splitting constants will be the mean of those from apical and equatorial Me*O ligands.

Both direct and indirect approaches thus show that exchange of apical and equatorial alkoxy groups in $(RO)_4P\cdot$ is extremely rapid. Decay by β-scission of the phosphoranyl radical † $\overline{OCH_2CH_2O\dot{P}(OBu^t)OPe^t}$ (see Scheme 1) was monitored by kinetic e.s.r. spectroscopy,[2,7,15] and the rate constant (identical for the radical derived from the two sources) is given by $\log(k/s^{-1}) = 10.8 - 31.7/\theta$, whence k (273 K) $= 5.4 \times 10^4$ s^{-1}. Even the acyclic radical $(Bu^tO)_4P\cdot$ undergoes β-scission slowly [2] [k (273 K) 9.5×10^4 s^{-1}] with respect to apical–equatorial ligand exchange. Tetra-alkoxyphosphoranyl radicals containing only primary or secondary alkyl groups will undergo β-scission much more slowly [*e.g.*[1] for $(EtO)_4P\cdot$, k (273 K) $= 3 \times 10^2$ s^{-1}].

We conclude that memory effects will not in general be detectable in phosphite oxidation, because of rapid equilibration of the possible isomers of the intermediate phosphoranyl radical. Only when β-scission is extremely rapid might it become possible to observe such an effect, and here a trigonal bipyramidal phosphoranyl radical may perhaps not be formed [see section (e)].

The spectroscopic parameters for the new phosphoranyl radicals reported in this work are given in Table 2.

(c) *Formation of Phosphoranyl Radicals.*—We have previously reported evidence which strongly favours cleavage of an apical, rather than an equatorial, P–C bond during α-scission of alkylphosphoranyl radicals [equation (xi; X = alkyl)].[12] Evidence of similar site-selectivity was obtained for aminophosphoranyl radicals [equation (xi; X = R_2N)].[12]



The reverse of reaction (xi), phosphoranyl radical formation, should also be site-selective with the incoming radical taking up an apical ligand site. Sulphuranyl radicals, $X_3\ddot{S}\cdot$, are closely related to phosphoranyl radicals and we have shown that addition of a methoxyl radical to dimethyl sulphoxylate is site-selective, such that the incoming radical becomes an ' apical ' ligand in the sulphuranyl adduct [equation (xii)].[4]

γ-Irradiation of trimethyl phosphite in methanol at 77 K apparently gives rise to the phosphoranyl radical (16a) rather than the more stable isomer (16b).[16] If $(MeO)_3\dot{P}H$ is formed by capture of a hydrogen atom by trimethyl phosphite, this result provides further experimental evidence for apical entry. However, the methoxy

† Measurements were made between 193 and 233 K. Only one signal was apparent and thus either the isomers (2a and b) are interconverting rapidly on the e.s.r. time scale or their spectra are indistinguishable because of overlap.

[15] K. Adamic, D. F. Bowman, T. Gillan, and K. U. Ingold, *J. Amer. Chem. Soc.*, 1971, **93**, 902.
[16] M. C. R. Symons, *Mol. Phys.*, 1972, **24**, 885; 1974, **27**, 785.

ligands may be equivalent in the species detected, with local C_{3v} symmetry at phosphorus and the unpaired

rate constants for first-order decay of the phosphoranyl radicals (18)—(21).

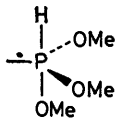
TABLE 2

E.s.r. parameters in cyclopropane solvent for the new phosphoranyl radicals described in this work

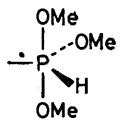
Radical	T/K	g-Factor [a]	Hyperfine splittings (G) a(P) [a]	Others
(2; R^1 = Bu^t, R^2 = Pe^t)	180	2.002	903	*b*
(2; R^1 = Bu^t, R^2 = Pr^iMe_2C)	210	2.002	904	*b*
(3)	260	2.003	888	
$\overline{OCH_2CH_2O}\dot{P}(OEt)O$-cyclo-$C_5H_9$	253	2.002	904	*a* (2 H) 1.8
(5; R = Me_3Si)	195	2.0018	958.6	*a* (1 H) 4.2
$(MeO)_4P\cdot$	220	2.0017	886.3	
$(MeO)_3\dot{P}OMe^*$ (7)	220	2.002	885	*a* ($1^{13}C$) 1.0
$(Me^*O)_3\dot{P}OMe$ (8)	220	2.002	886	*a* ($3^{13}C$) 1.0
(9; R^1 = R^2 = Me)	254	2.002	910	*a* (2 H) 1.7
(9; R^1 = Me, R^2 = Me*)	253	2.002	911	*a* (2 H) 1.7; *a* ($1^{13}C$) 0.9
(9; R^1 = R^2 = Me*)	253	2.002	910	*a* (2 H) 1.7; *a* ($2^{13}C$) 0.9
(12) [c]	263	2.003	986	*a* ($1^{13}C$) 4.5
(13)	253	2.002	894	*a* (1 H) 5.1; *a* ($1^{13}C$) 3.4
(15)	263	2.002	1 036	*a* (1 H) 4.0
(20)	196	2.0022	890.6	
(21)	203	2.0022	912.8	*a* (1 H) 3.4
(23) [d]	200	2.003	970	

[a] Obtained using the Breit–Rabi equation. *g* Factors quoted to four decimal places and phosphorus splittings quoted to one decimal place are considered accurate to ±0.0002 and ±0.5 G, respectively: others are probably accurate to ±0.001 and ±1—2 G respectively. [b] No further fine structure detectable; peak–peak linewidth *ca.* 5 G. [c] In cyclopropane–toluene (1 : 1 v/v). [d] In toluene.

electron confined to a σ*-P–H orbital [16] rather than distributed over H, P, and an apical methoxy ligand as in the trigonal bipyramidal structure (16a) [see section (e)].



(16a)



(16b)

Recent molecular orbital calculations of the potential energy surface for reaction (xiii) suggest that the incoming hydrogen atom takes up an apical ligand site in (17).[17] However, no barrier was detected for the α-scission of (17) [reverse of reaction (xiii)], although this

$$H\cdot + PH_3 \longrightarrow H_4P\cdot \quad (17) \quad (xiii)$$

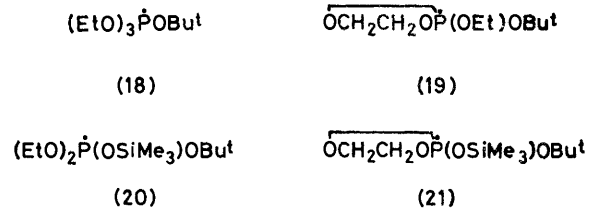
radical is clearly reasonably stable towards fragmentation.[18]

(d) *Site-selectivity in β-Scission.*—Although it appears that rapid exchange of alkoxy ligands will, in general, prevent the detection of a memory effect in phosphite oxidation, it still remains to determine whether or not the β-scission process is site-selective. We have searched for this selectivity by making use of the known preference of the five-membered ring to bridge apical and equatorial sites in phosphoranyl radicals derived from 1,3,2-dioxaphospholans,[7,8] and the expected higher apicophilicity of the Me_3SiO group compared with that of Bu^tO.

Using kinetic e.s.r. spectroscopy we have measured the

[17] J. M. Howell and J. F. Olsen, *J. Amer. Chem. Soc.*, 1976, **98**, 7119.

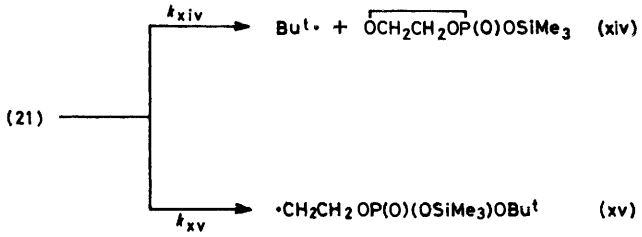
The t-butyl radical was the only alkyl radical detected as a β-scission product from (18)—(20), but (21) gave rise



(18) (19)

(20) (21)

to both $Bu^t\cdot$ and radical (22) [$a(2H_\alpha)$ 22.0, $a(2H_\beta)$ 28.2 G at 270 K]. The observed first-order rate constants were independent of the incident light intensity and correspond to those for β-scission.[2] The radical concentration ratio $[Bu^t\cdot] : [(22)]$ at each temperature was taken to



(22)

equal $k_{xiv} : k_{xv}$, since the rate constants for removal of both these radicals should be similar.[19] Between 253 and 293 K $[Bu^t\cdot] : [(22)]$ was 2.4 ± 0.2. The results are gathered in Table 3.

The relative apicophilicity of EtO and Bu^tO groups is

[18] A. J. Colussi, J. R. Morton, and K. F. Preston, *J. Chem. Phys.*, 1975, **62**, 2004.

[19] D. Griller and K. U. Ingold, *Internat. J. Chem. Kinetics*, 1974, **6**, 453.

not known with certainty, although the apicophilicities of endocyclic CH_2O and CMe_2O groups are similar in phosphoranyl radicals of the type $\dot{O}CH_2CMe_2OPX_2$.[8] The interconversions shown in equations (xvi)—(xviii)

TABLE 3

Rate constants and activation parameters for the decay of phosphoranyl radicals in cyclopropane solution

Radical	T/K	$\log_{10}(A/s^{-1})$ [a]	E_a [a]/ kJ mol	k/s^{-1} at 233 K
(18)	193—223	10.6 [b]	32.2 [b]	2.6×10^3
(19)	193—225	10.4	34.3	5.1×10^2
(20)	225—251	11.0	33.7	2.5×10^3
(21)	231—258	10.5 [c]	38.1 [c]	9.1×10^1 [c]
(23) [d]	205—230	13.3	43.8	3.0×10^3

[a] Estimated errors in log A and E_a ± 1.0 and ±4 kJ mol^{-1}, respectively. [b] $\log_{10}(A/s^{-1})$ 10.3 and E_a 31.4 kJ mol^{-1} have been reported previously [2] in propane solvent. [c] Values refer to decay by β-scission to form t-butyl radicals. [d] In toluene solvent.

are expected to occur rapidly compared with β-scission [see section (c)] and the equilibrium constants should be similar for each pair of isomers.*

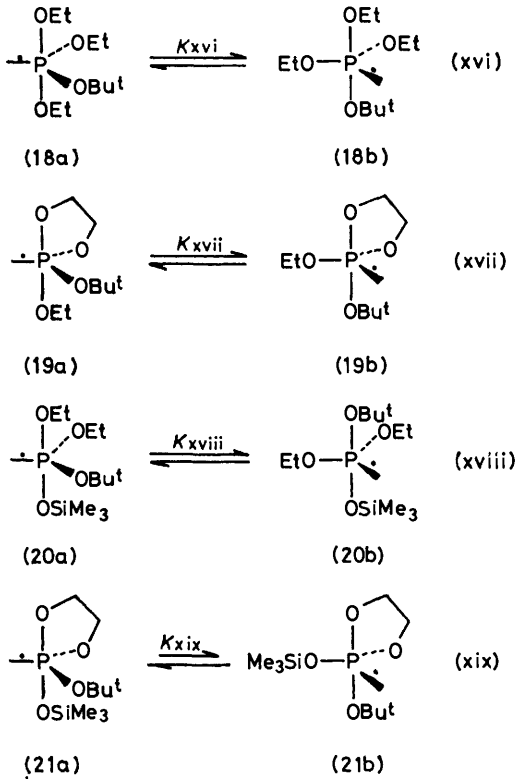
Thus, the t-butoxy group has ready access to both apical and equatorial sites in (18)—(20). The e.s.r. spectrum observed for (21) shows the splitting from one ring proton † [a(H) 4 G] expected [8] if the apicophilicities of Me_3SiO and Bu^tO groups are appreciably different (see Figure 1). In view of the higher group electronegativity expected for Me_3SiO it may be assumed that this ligand has the higher apicophilicity, and that the radical exists predominantly as one isomer, (21a). Access of Bu^tO to the equatorial site is thus restricted for (21).

The radical (19) undergoes β-scission five times more slowly than (18) at 233 K, and this difference may be attributed to the presence of the five-membered ring in the former radical. However, the radical (21) undergoes β-scission to give Bu^t· 27 times more slowly than (20). We suggest that the rate difference for (20) and (21) is too large to be accounted for solely by the presence of the ring in the latter, and may be taken as evidence for *apical site-selectivity in β-scission.*

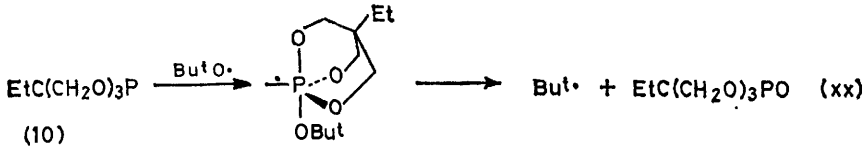
We concede that the above argument is based on relatively small rate differences and is not unequivocal, although other evidence also supports apical site-selectivity. Thus, β-scission with ring opening occurs in competition with t-butyl radical formation for (21) *but not for* (19).[1] If the t-butoxy group in (21) had free access to the favoured site for β-scission, it seems unlikely that ring cleavage would occur in competition with t-butyl radical formation, and thus apical site-selectivity is again indicated.

* If only statistical factors are considered then $K_{xvi} = K_{xvii} = 0.5K_{xviii}$. Only one e.s.r. signal was observed for (18)—(21).

Provided that the phosphoranyl radical produced by addition of Bu^tO· to (10) has a trigonal bipyramidal



skeleton, the t-butoxy group must occupy an apical site as shown in (23), since a six-membered ring cannot bridge apical positions. At 233 K, the radicals (18) and (23)



undergo β-scission at similar rates although the activation parameters for fragmentation of (23) are markedly different from those for (18)—(21). This result is consistent with, but does not require, apical site-selectivity and is evidence against marked equatorial site-selectivity in β-scission.

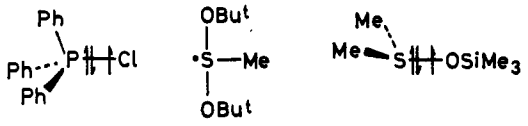
In summary, β-scission is probably site-selective and involves an apical alkoxy ligand. However, on the basis of the present results, it is not possible to determine the degree of preference for the apical site.

(e) *Conclusions.*—In this section we attempt to draw together the conclusions from the preceding sections and suggest a unified scheme for formation, permutational isomerism, and fragmentation of phosphoranyl radicals.

Most phosphoranyl radicals detected by e.s.r. spectroscopy appear to possess the quasi-trigonal bipyramidal (TBP) structure, in which the unpaired electron is in an

† The spectrum still exhibits a doublet splitting up to the highest temperature examined (283 K).

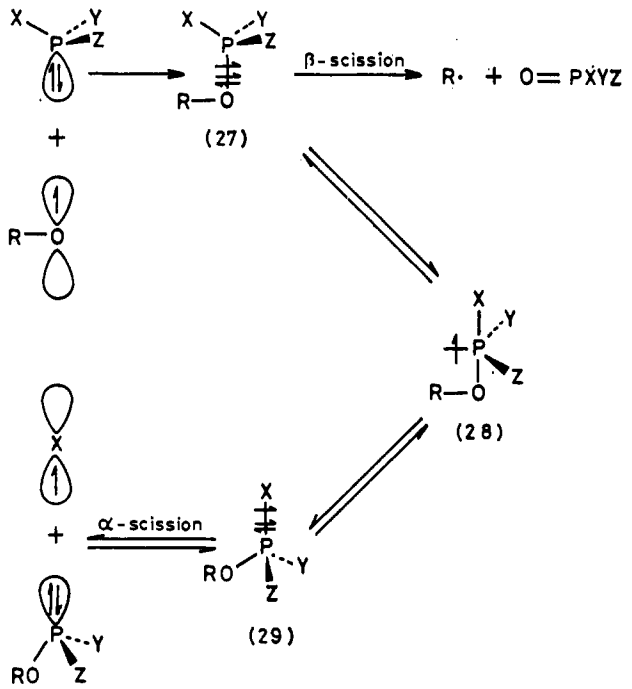
orbital centred mainly on phosphorus and the two apical ligands.[8,20,21] However, it has recently been shown [22,23] that the anisotropic e.s.r. spectra of certain monohalogenophosphoranyl radicals [*e.g.* $Ph_3\dot{P}Cl$ [22] and $(MeO)_2\dot{P}(Br)\dot{S}$ [23]] indicate that the unpaired electron is confined to a σ*-P–Hal orbital with local C_{3v} symmetry at phosphorus as shown in (24).



(24) (25) (26)

Furthermore, whilst $Me\dot{S}(OBu^t)_2$ possesses the 'T shaped' structure (25), with two equivalent S–O bonds,[24] the *S*-methyl groups in $Me_2\dot{S}OSiMe_3$ appear to be equivalent,[25] consistent with the unpaired electron in the latter radical being in a σ*-S–O orbital as shown in (26).

We suggest that a σ*-type phosphoranyl radical may be formed initially when an alkoxyl radical adds to the phosphorus compound PXYZ, and that this initial adduct

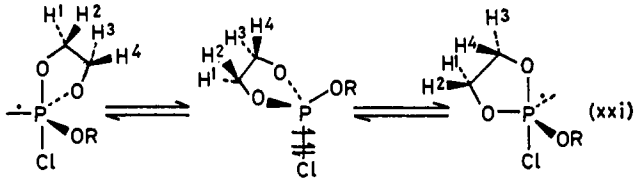


SCHEME 3

usually rearranges to the TBP-type when the latter is more stable. The TBP-form could then undergo ligand exchange and fragmentation through the intermediacy of the σ*-form. These proposals are summarised in Scheme 3.

The interaction of the SOMO of RO· with the HOMO (lone-pair) orbital of PXYZ leads to the σ*-form (27), which may undergo β-scission or (reversibly) transform to the TBP-form (28) *in which* RO *becomes an apical ligand*. Exchange of X, Y, and Z in (28) may occur by interconversion with (27). The TBP-form (28) can also collapse to the σ*-form (29) in which the *apical* ligand X becomes part of the three-electron bond. The σ*-form (29) may revert to a TBP-form (allowing exchange of Y, Z, and RO) or may undergo α-scission with loss of X·. α-Scission will often be reversible, although loss of RO· from (28) *via* (27) is probably energetically unfavourable.[26]

Scheme 3 provides an internally consistent explanation for apical site-selectivity in formation, α-scission, and β-scission of phosphoranyl radicals, as well as for the observed [8] mode of ligand exchange. The relatively high rate [8] of the M4 (ring) exchange shown in equation (xxi) may be explained in terms of the ready accommodation of the unpaired electron in the σ*-P–Cl orbital of the intermediate (30).



(30)

In terms of Scheme 3, it is possible that the TBP-form (28) is not formed to an appreciable extent from (27), if β-scission of the latter is extremely rapid. In such systems a large memory effect might be observable.

The e.s.r. spectra of two isomeric phosphoranyl radicals have been detected simultaneously in the same sample for a number of species containing dialkylamino ligands.[7] One of these isomers is characterised by a relatively low value of a(N) and a normal * value of a(P). The other isomer shows a high value of a(N) and an abnormally low value of a(P). For example,[7] the two isomers of $Me_2N\dot{P}(OEt)_2OBu^t$ exhibit a(N) 2.8, a(P) 841 G and a(N) 12.7, a(P) 697 G, respectively. We have previously assigned both these spectra to TBP-forms; the species showing the lower nitrogen splitting was thought to have an equatorial amino ligand, and that with the larger splitting an apical amino ligand.[7] An alternative, but perhaps less likely, assignment would be that the isomers exhibiting the large values of a(N) might be better described as σ*-forms [21,23] with the unpaired electron in an anti-bonding P–N orbital and with (approximately) local C_3 symmetry at phosphorus. The important difference between the isomers showing low or high values

* By 'normal' we mean expected on the basis of the electronegativity of the ligands about phosphorus.[8]

[20] T. Gillbro and F. Williams, *J. Amer. Chem. Soc.*, 1974, **96**, 5032.

[21] K. Nishikida and F. Williams, *J. Amer. Chem. Soc.*, 1975, **97**, 5462.

[22] T. Berclaz, M. Geoffroy, and E. A. C. Lucken, *Chem. Phys. Letters*, 1975, **36**, 677.

[23] M. C. R. Symons, *Chem. Phys. Letters*, 1976, **40**, 226.

[24] W. B. Gara, B. P. Roberts, C. M. Kirk, B. C. Gilbert, and R. O. C. Norman, *J. Chem. Research*, 1977, 152 (S), 1748 (M).

[25] W. B. Gara and B. P. Roberts, *J. Organometallic Chem.*, 1977, **135**, C20.

[26] W. G. Bentrude and R. A. Wielesek, *J. Amer. Chem. Soc.*, 1969, **91**, 2406; W. G. Bentrude, J. H. Hargis, N. A. Johnson, T. B. Min, P. E. Rusek, jun., H.-W. Tan, and R. A. Wielesek, *ibid.*, 1976, **98**, 5348.

of a(N) is that the former have two-electron P–N bonds, whereas the latter do not. Our earlier conclusion [7] remains, that the two-electron (equatorial) P–N bond undergoes cleavage indirectly, by way of an isomer (σ^* or TBP-type) in which the P–N bond order is less than unity and there is relatively high spin density on nitrogen.

EXPERIMENTAL

E.s.r. Spectroscopy.—The techniques employed for the detection of e.s.r. spectra during continuous u.v. irradiation of samples in the cavity of the spectrometer have been described previously.[7,27] The kinetics of radical removal were measured by computer-averaging of a large number of e.s.r. signal decay curves produced by positioning a rotating sectored disc in the light path.[7,15] Samples were prepared using a standard vacuum line and sealed under vacuum in Suprasil quartz tubes (4 mm o.d.). The solutions were *ca.* 1M in peroxide (or dimethyl sulphoxylate) and *ca.* 0.5—1M in phosphite. In the experiments designed to detect memory effects, the ratio of alkyl radical concentrations was not changed by doubling the phosphite concentration. Relative radical concentrations were determined by electronic integration of the derivative spectrum, followed by manual integration of the absorption curve obtained. Simulation of spectra, including the effects of exchange, was accomplished using the program ESREXN written by Dr. J. Heinzer and obtained from QCPE (program No. 209).

Materials.—Di-t-butyl peroxide was obtained commercially and purified before use. Diethyl,[28] di-t-pentyl,[29] dicyclopentyl),[30] bis-(1,1,2-trimethylpropyl),[31] and bis-(trimethylsilyl) [32] peroxides were synthesised by literature methods.

Dimethyl Sulphoxylate.—Although this compound has been reported previously,[33-35] it does not appear to have been adequately characterised. Almost certainly the material of b.p. 47—48 °C at 36 Torr obtained by Christ *et al.*[34] was dimethyl sulphite, rather than the sulphoxylate. Dry methanol (4.8 ml) was added during 5 min to a rapidly-stirred suspension of di-imidazol-1-yl sulphide [36,37] (*ca.* 80% pure; 10 g) in n-pentane (25 ml) under dry nitrogen. The mixture was stirred vigorously for a further 20 min, cooled in an ice–salt bath, and imidazole removed by filtration. Distillation of the filtrate yielded *dimethyl sulphoxylate*, b.p. 26 °C at 120 Torr (65—66 °C at 755 Torr), as a liquid (Found: C, 25.8; H, 6.6; S, 33.9%; *m/e* 94.0088. $C_2H_6O_2S$ requires C, 25.5; H, 6.4; S, 34.1%; *M*, 94.0091).

^{13}C-Labelled dimethyl sulphoxylate was prepared by a small-scale modification of the above procedure. Methanol (200 μl; 96 atom % ^{13}C) was added by syringe to a suspension of di-imidazol-1-yl sulphide (80% pure; 0.6 g) in n-hexadecane (1.5 ml) and the mixture was shaken vigorously for 15 min at room temperature. Using a vacuum line, all material volatile at room temperature and 0.1 Torr was distilled on to anhydrous lithium chloride (0.05 g). After shaking vigorously for 3—4 min dimethyl sulphoxylate was distilled into a storage tube (yield *ca.* 100 μl).

2-(1,1,2-*Trimethylpropoxy*)-1,3,2-*dioxaphospholan.*—Methyl-lithium (45 ml of a 2.18M solution in ether) was added dropwise during 10 min with stirring and cooling (ice-bath) to a solution of 2,3-dimethylbutan-2-ol (9.8 g) in ether (50 ml). 2-Chloro-1,3,2-dioxaphospholan (11.5 g) was added dropwise with stirring and cooling (ice-bath) to the resulting solution. The mixture was stirred for a further 30 min at room temperature, the precipitated lithium chloride removed by filtration, and the ether removed under reduced pressure. Distillation of the residual oil yielded the product, b.p. 44 °C at 0.2 Torr (Found: C, 50.4; H, 9.0; P, 15.8. $C_8H_{17}O_3P$ requires C, 50.0; H, 8.9; P, 16.1%).

2-*Cyclopentoxy*-1,3,2-*dioxaphospholan* was prepared from cyclopentanol and 2-chloro-1,3,2-dioxaphospholan in ether with triethylamine as the tertiary base, b.p. 60—61 °C at 0.1 Torr (Found: C, 47.8; H, 7.4; P, 17.6. $C_7H_{13}O_3P$ requires C, 47.7; H, 7.4; P, 17.6%).

2-*Trimethylsiloxy*-1,3,2-*dioxaphospholan* was prepared similarly from trimethylsilanol,[38] 2-chloro-1,3,2-dioxaphospholan, and triethylamine in ether at −20 °C, b.p. 60—61 °C at 14 Torr (Found: C, 33.6; H, 7.4; P, 17.2. $C_5H_{13}O_3PSi$ requires C, 33.3; H, 7.3; P, 17.2%). The 4,4-*dideuterio analogue* was prepared from 2-chloro-4,4-dideuterio-1,3,2-dioxaphospholan.[8] Diethyl trimethylsilyl phosphite was prepared in a similar way from diethyl chlorophosphite, trimethylsilanol, and triethylamine, b.p 60—62 °C at 15 Torr (lit.,[39] 60—62 °C at 11 Torr).

The ^{13}C-labelled phosphites $(^{13}CH_3O)_3P$ and $\ulcorner OCH_2CH_2OPO^{13}CH_3\lrcorner$ were prepared by small scale reactions of phosphorus trichloride or 2-chloro-1,3,2-dioxaphospholan, respectively, with methanol (96 atom % ^{13}C; 200 μl) and *NN*-diethylaniline in n-hexadecane with vigorous stirring (the methanol is not completely miscible). The phosphites were then distilled from the reaction mixture at room temperature under high vacuum.

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